

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

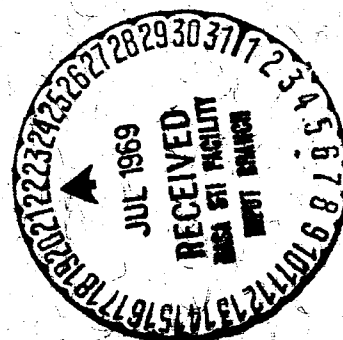
X-735-69-230

REPRINT

NASA TM X-63595

PRIMARY CHEMICAL, METALLURGICAL, AND ELECTRO-OPTICAL TECHNIQUES FOR EVALUATING MAGNETIC TAPES

JUNE 1969



GODDARD SPACE FLIGHT CENTER

GREENBELT, MARYLAND

N69-30755

FACILITY FORM 602

(ACCESSION NUMBER)

54

(PAGES)

TMX-63595

(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

(CATEGORY)

X-735-69-230

**PRIMARY CHEMICAL, METALLURGICAL, AND
ELECTRO-OPTICAL TECHNIQUES FOR
EVALUATING MAGNETIC TAPES**

**Aaron Fisher
John Grimsley
Thomas Sciacca
Charles Staugaitis**

**Materials Research and Development Branch
Systems Division**

June 1969

**GODDARD SPACE FLIGHT CENTER
Greenbelt, Maryland**

PRECEDING PAGE BLANK NOT FILMED.

FOREWORD

This report, a compilation of the total Materials Research and Development Branch analytical experience as applied to magnetic tape, is the result of an investigation into what type of tests could provide meaningful differentiating criteria relative to tape characteristics.

Various infrared (IR) analytical techniques and modifications will be useful. Although examination has shown that two thermal methods, DTA and DSC, are promising, thermal mechanical analysis has been refractory. TGA has not yet been explored.

Investigation of a variety of metallographic techniques showed that all were useful for studying tape characteristics. Observations from mechanical tests, including surface-roughness and tensile tests, readily showed up differences between tapes. Hardness tests proved unreliable and inaccurate for evaluating tape binders.

Replicating techniques can be used to classify adhesion characteristics of the magnetic oxide or binder system. Oxide particles are measurable in the sub-micron range. Unusual or unsuspected metallo-organic additives may become apparent in emission-spectrographic studies on the binder.

PRECEDING PAGE BLANK NOT FILMED.

CONTENTS

	<u>Page</u>
FOREWORD	iii
INTRODUCTION	1
PRIMARY CHEMICAL ANALYSIS	1
Infrared, Ultraviolet, and Visible Spectrophotometry	1
Attenuated Total Reflectance Spectroscopy	1
Infrared Pyrolyzate Examination.	2
Vacuum Polymer Heating with Thermal-Gradient Condensation	2
Vacuum Condensable Materials (VCM) Apparatus	2
Pyrolysis Gas Chromatography	3
Differential Thermal Analyzer (DTA)	3
Thermogravimetric Analysis (TGA)	4
Differential Scanning Calorimeter (DSC)	4
Thermo-Mechanical Analysis (TMA)	4
Binder-Oxide System Removal	5
Binder-Oxide System Ashing	5
Extractions	5
METALLOGRAPHIC, MECHANICAL, AND RELATED PROCEDURES FOR THE INVESTIGATION OF MAGNETIC TAPES AND HEADS . .	6
Metallographic Techniques	6
Low-Magnification Techniques (1X to 100X)	6
High-Magnification Techniques (100X to 30,000X or Higher) . . .	6
Preparation of Tape Cross-Section Specimens	8
Head-Tape Compatibility Tests	8
Blocking Tests	9
Mechanical Tests	9
Tensile Tests	9
Hardness Tests	10
Surface-Roughness Measurement	10

CONTENTS (Continued)

	<u>Page</u>
ELECTRON MICROSCOPE, X-RAY, AND OTHER ANALYTICAL PROCEDURES FOR THE INVESTIGATION OF MAGNETIC TAPE	10
X-Ray Diffraction Analysis	11
Electron-Diffraction Analysis	11
Electron Microscopy	11
Preferred Orientation	12
Emission Spectroscopy	12
RECOMMENDATIONS	12
CONCLUSION	12
SOURCES	13
REFERENCES	13
APPENDIX A - INTERIM REPORT ON CHEMICAL CHARACTERI- ZATION OF 3-M 551 MAGNETIC TAPE	15

ILLUSTRATIONS

<u>Figure</u>	<u>Page</u>
1 Typical Infrared Traces of Complete RCA Tape 617 and Binder Separated from Memorex 62-2	17
2 Typical ATR Spectrum of Mylar Tape, Front and Back . .	18
3 Comparative ATR Spectra of Cured Polyurethane and Kapton Film	19
4 Infrared Pyrolyzate Spectra of RCA 617 Tape Binder and Known Urethane	20
5 Infrared Spectra of 3-M 551 Tape Binder, Vacuum Heated and Vapors Condensed in a Thermal-Gradient Tube	21

ILLUSTRATIONS (Continued)

<u>Figure</u>		<u>Page</u>
6	Infrared Spectra of Binder Vacuum Condensables as a Function of Known Temperature Treatment	22
7	Typical Pyrolysis Gas Chromatograms of RCA 617 Tape and Binder	23
8	Differential Thermal Analysis Trace of 3-M 551 Binder . .	24
9	Differential Scanning Calorimeter Trace of 3-M 551 Binder	25
10	Differential Scanning Calorimeter Trace of γ Fe ₂ O ₃	26
11	Low-Magnification Appearance of Tape-Recorder Heads After Use	27
12	Photograph of As-Polished Tape-Recorder Head Showing Voids in Potting Material and Surface Finish of Head . . .	28
13	Photographs of 3-M 551 Magnetic Tape, Before and After Being Run 17,000 Cycles Over Brass Recorder Heads on a Continuous-Loop Tape Machine	29
14	Appearance of Brass Magnetic Recorder Heads After Use with 3-M 551 Tape	30
15	Appearance of 3-M 551 Tape, Tape in Virgin Condition, and Tape After Run of 17,000 Cycles on a Continuous-Loop Tape Machine	31
16	Brass Magnetic Head After Test with 3-M 551 Tape	32
17	Cross-Section of 3-M 551 Tape Showing Artificial Defect Made with a Steel Scribe	33
18	Cross-Section Specimens of Magnetic Tapes	34
19	Head/Tape Compatibility Tests	35
20	Photographs of Irradiated RCA 617 and 3-M 551 Tape Tensile Test Specimens After Being Tested	36
21	Representative Tape Smoothness Profiles	37
22	Graphite Particles Extracted from RCA 617 Tape	38
23	Replicas of Tapes at Various Magnifications	39

ILLUSTRATIONS (Continued)

<u>Figure</u>		<u>Page</u>
24	Examples of Surface Defects in RCA 617 Tape	40
25	Thin Section of RCA 617 Tape as Received	41
26	Particles Extracted from Various Tapes (a through d)	42
26	Particles Extracted from Various Tapes (e through h)	43
26	Particles Extracted from Various Tapes (i and j)	44

TABLES

<u>Table</u>		<u>Page</u>
1	Observations on Binder Solubility	45
2	Basic Tape Characteristics	46
3	Major Diffraction Lines Common to γ -Fe ₂ O ₃ and Fe ₃ O ₄ . .	47
4	Data Obtained from Examination of Oxide Particles	47
5	Comparative Emission Spectrographic Analysis of Iron Oxide Separated from RCA 617 Binder and Iron Oxide in Combination with 617 Binder	48

PRIMARY CHEMICAL, METALLURGICAL, AND ELECTRO-OPTICAL TECHNIQUES FOR EVALUATING MAGNETIC TAPES

INTRODUCTION

Spacecraft recorders and tape systems must be very reliable and long lived because they are direct communication links between the ground observer and experiments on unmanned spacecraft. A recent survey of the recorder and tape industry indicates that many problems, including tape-head sticking, have not been solved. A program was set up using various physico-chemico-metallurgical techniques to search for those criteria that could be especially significant for differentiating between tapes. The following reviews the attempted methods and the analytical success of each.

PRIMARY CHEMICAL ANALYSIS

It is important that analytical methods be developed to find tape differences critical to good and bad tape performances. In the chemical analysis of magnetic tapes, emphasis has been placed on investigation of techniques inherently capable of producing under known conditions primary, stable, recognizable, and repeatable signatures, attributable to a basic material property. Some techniques have proved fruitful; blind alleys have been indicated.

Infrared, Ultraviolet, and Visible Spectrophotometry

These techniques depend on the fact that certain groups of atoms absorb energy at or near the same frequency, regardless of the structure of the rest of the molecule that they may be a part of. The spectra bands of these energy absorptions are clues to the overall structure of the molecule. Spectra have been obtained of the tape backing or carrier (normally mylar) after all binder-oxide coating or graphite surface lubricant has been removed. Infrared spectra have been obtained of the oxide-binder system alone, after it was stripped from the mylar carrier. Even though the binder is filled mainly with oxide particles, identification of general classes of binder materials is possible (Figure 1). Binder extracts of pure phase isolates may be identified.

Attenuated Total Reflectance Spectroscopy

This analytical method, a modification of the infrared technique, examines the clean surface of the tape backing for clues to the tape chemistry. The binder does not have to be removed; however, all graphitic lubricants on the back side

of continuous-loop tapes should be cleaned away before analysis. This method provides information on any coating deposited on the magnetic layer or any other non-highly filled coating or film. If filler contents exceed 4 percent, this method is not effective. Figures 2 and 3 show typical traces.

Infrared Pyrolyzate Examination

This type of examination is the analysis of gaseous condensables resulting from the high temperature degradation of organic or polymer products. Using library standards of such volatile condensables or fingerprints, the analyst can compare and ascertain the major original polymer components of the tape. Because only condensed vapor volatiles are examined, inorganic filler materials do not interfere (carbon and the magnetic oxide fillers are of no concern). Figure 4 shows a typical trace. This technique has been used successfully to identify or confirm major chemical characteristics of the binder, but the technique is too insensitive for analysis of trace materials. This is unfortunate, because trace compounding ingredients in the binder could be an important part of the contact surface chemistry at the tapehead. Other techniques, modifications of the foregoing, are being adapted to the collecting of special fractions of condensable outgassing products. These techniques use variations in heating temperature and condensable cooling in a vacuum environment.

Vacuum Polymer Heating with Thermal-Gradient Condensation

This technique attempts to separate for further analysis the various volatile components which may make up the binder layer. Binder material 551 was heated in a flask at 350° F and 10^{-3} torr. The volatiles condensed into three separate, well defined, yellowish rings, throughout a long glass tube having a designed uniform thermal gradient. This tube was hot at the flask side and comparatively cool at the pump side. Infrared traces of the three condensates indicated that they were basically similar, low molecular weight, polyester urethanes with some slight molecular end-group variations (Figure 5). Similarly, our polymer outgassing-system operation has been modified for possible analytical input.

Vacuum Condensable Materials (VCM) Apparatus

This operation, normally carried out for 24 hours at 10^{-6} torr vacuum and 125° C, can provide an overall weight loss and a condensable vapor loss. A cooling plate, maintained at room temperature, is weighed before and after heating to determine the weight of the condensable vapor loss. A salt flat to help provide infrared-analysis information can be substituted for the condensing plate. Besides being capable of obtaining condensables for IR study at 125° C, this

instrumentation can provide condensables, if extant, at 50° C, 75° C, and 100° C. Testing is done at the lower temperatures to provide clearer IR traces of individual compounds. (At lower temperatures a compound or condensable normally evolving at 100° C could not complicate interpretation of an IR trace of a material evolving at 75° C (Figure 6).)

Pyrolysis Gas Chromatography

This complex technique is undoubtedly one of the most sensitive methods for providing material fingerprints. This system of analysis provides a graph of a varied number of peak heights against a time base. It can be used effectively to show minute chemical changes, if any result from tape wear or ageing in ambient or modified environments. Comparison would have to be against a reference standard of virgin tape. Such a complicated operation, however, would require system computerization. Figure 7 shows a typical run.

Attempts at column chromatography and similar separation techniques were inconclusive. Normal gas chromatography is not very useful in tape work because it requires a higher vapor pressure than any of the components normally present in the organic phase of the tape. However, gas chromatography may be effective in determining the presence of residual or reabsorbed solvents which could increase undesirable tape sticking.

In the foregoing techniques, the analysis depends primarily on qualifying various molecular species in the final determination of unknowns. Binder analysis has also been attempted based on binder-oxide deformation as a function of load and temperature. Exothermic- or endothermic-temperature developments were observed within the binder-oxide system under the influence of either a uniform temperature increase or a temperature environment kept constant over a period of time. Some of the thermal analytical tests and their possible effectiveness are described in the following.

Differential Thermal Analyzer (DTA)

The DTA charts the various exotherms or endotherms which a material experiences as its temperature is increased at a known rate. The plot shows differential temperature variations between the material under investigation and an inert alumina sample, both having been heated at the same rate and correspondingly thermocoupled. When the binder-oxide system of 551 tape was subjected to this technique, characteristic double exotherm peaks were found at approximately 350° F and 465° F; these peaks are indicative of temperature variations occurring when this particular binder species undergoes degradation (Figure 8).

Careful examination of the graph and its expansion or technique refinement may indicate the onset of further cross-linking, moisture loss, or residual solvent loss, if these changes occur.

Thermogravimetric Analysis (TGA)

TGA is a graph of weight loss continuing with rise in temperature. It can show the relative stability of binders, indicate the presence of unusual additives or moisture, or demonstrate weight-loss idiosyncrasies. It can very easily confirm or corroborate other observations in the DTA.

Differential Scanning Calorimeter (DSC)

The DSC maintains a sample temperature isothermal at the same temperature as a reference source, while both are being programmed through a prescribed heating rate. The calorimeter compares temperatures during programming and supplies to either the sample or reference that heat energy required to maintain isothermal conditions. The amount of energy required to maintain these isothermal conditions through endothermal or exothermal excursions is recorded as a function of time (temperature). The area under various developed peaks is directly proportional to the heat energy absorbed or liberated in the transition or required for maintenance of the dynamic isothermal programming. This technique has been used to confirm the identity of the 551 tape backing as mylar. Exotherm peaks of the DTA (Figure 8) are easily confirmed on the DSC (Figure 9) and are determined to be characteristic of the urethane alone, because no calorimetric changes are noted for the γ Fe₂O₃ at 350° F and 465° F. The γ Fe₂O₃ peaks at 410° F (Figure 10). The γ Fe₂O₃ is normally used as the magnetic oxide in the binder-oxide system.

Thermo-Mechanical Analysis (TMA)

TMA can be useful in determining the softening point of a polymeric material under load. As much as several hundred grams of force may be used on the sample through a stylus or penetrometer of 0.025-inch radius. Test attempts on a sample of tape with binder intact have been difficult, even under maximum loading and with the use of a smaller radius stylus. Present attempts are directed towards increasing the nominal 0.0002-mil thick magnetic coating sample size to 0.005 inch, testing apart from the mylar carrier, and elevating the temperature range.

The foregoing techniques used to operate on the tape or binder-oxide system, permit some basic phenomena or binder characteristics to be readily observed, analyzed, compared, and/or categorized. Some secondary preparative and experimental operations are also very important.

Binder-Oxide System Removal

Many magnetic coatings can be easily removed if immersed in 50 percent KOH at about 150° F. Acetone has been used successfully to remove RCA binders, numbers 583, 593, 606, 617, and 41-32 (Table 1). Minnesota Mining and Manufacturing binders are generally more resistant to removal and solution. The RCA binders can generally be dissolved in dimethylformamide in 0 to 15 minutes at 100° F to 125° F to release carbon and magnetic oxide, if both are present. Magnetic oxide is easily separated with a magnet; the carbon is separated by centrifuging. Ashing is the primary method of recovering the oxide in the 3-M binders. Ashing should be done in a carbon analyzer to facilitate analysis for small amounts of graphite lubricant.

Binder-Oxide System Ashing

This operation is easily performed at 500° C to 600° C on either the magnetic coating or the whole tape (but the binder-oxide relationship is more desirable and useful). Oxide contents have ranged from approximately 67 percent to 81.6 percent (Table 2). Total filler contents may be higher if the entire carbon-black or graphite content is considered. Important tape behavior hinges on the binder-oxide or binder-filler ratio and oxide particle size. Some of the characteristics evolving from or dependent on the binder-filler weight ratio and overall particle surface area are: coating strength, elongation, hardness, abrasiveness, lubricity, blocking, roughness, potential for moisture and solvent absorption, total particle coverage, polymer-binding capability, tape-wetting capability during application, and final adhesion to carrier after bake out or curing. An oxide ratio increasing beyond the optimum would tend to degrade many of the characteristics in the foregoing.

Extractions

Soxhlet extractions can be performed on large quantities of binder to concentrate possible small percentages of unknown additives. Then the conventional classic organic and IR analysis can be performed on these concentrates. In this manner, a silicone lubricant was found in RCA tapes 853 and 617 after soxhlet extraction and a fluorescene dye in tape 551 after an alcohol extraction. The dye migrating from the tape was subsequently found to produce staining on brass-simulated tape heads at 150° F. Appendix A lists a general GSFC analytical procedure which also indicates the effectiveness of the solvent extractions.

The "Chemical Analysis of Magnetic Recording Tape"¹ is probably the only existing formalized procedure for general tape analysis. The article provides good background information on the qualitative aspects of tape components.

METALLOGRAPHIC, MECHANICAL, AND RELATED PROCEDURES FOR THE INVESTIGATION OF MAGNETIC TAPES AND HEADS

Following are techniques for studying the wear, friction behavior, and interfacial characteristics of magnetic tape and heads and an evaluation of the potential of these techniques in the study of magnetic tapes and heads.

Metallographic Techniques

Bench microscopes and macrographic and metallographic equipment were used to examine magnetic tapes and heads from 1X to 30,000X magnifications. The type and usefulness of the information obtained from these examinations depended on the technique, the magnification, and the sample used (whether tapes or heads were examined). Tapes and magnetic heads in both the virgin condition and after being tested in a continuous-loop magnetic-tape recorder were examined. Similarly, tapes and heads were examined that have been run on a machine specifically designed for this materials investigation. Details of the design and construction of the machine are presented in "Designs and Construction of a Magnetic-Tape Testing Machine."²

Low-Magnification Techniques (1X to 100X). Tapes and heads were examined at magnifications from 10X to 70X with a binocular zoom microscope. At these magnifications, the surface finish of the heads could be evaluated; gross imperfections such as voids in the head potting material, polishing pits, large inclusion, etc., were readily observed. After being run on the continuous loop recorder or the tape-testing machine, the heads were examined for wear, tape-tracking behavior, wrap-angle variations, evidence of tape-binder transfer to the head, and the nature (size, color, texture, etc.) of wear particles normally present on tested heads. Figures 11 and 12 show examples of low-magnification photographs of heads. Virgin tapes were examined at these magnifications to determine their characteristics before testing. Scratches and surface texture are the usual observations documented. After testing the presence of wear debris, additional scratches and other changes in the surface texture were usually observed. The nature of the wear debris on the tape surface (whether the debris is metallic or nonmetallic) can usually be established by low-angle lighting on the tape surface. Figure 13, photographed at low magnification, shows the appearance of the tape surface before and after testing on the continuous-loop machine. The binocular microscopes used in the detailed visual examinations have a depth of field and resolution superior to that of the monocular macrographic equipment used to obtain the photomacrographs in Figures 11 through 13.

High-Magnification Techniques (100X to 30,000X or Higher). Metallographs providing a choice of incident, darkfield, oblique, Nomarski interference, and

polarized illumination were used for examinations between 100X and 3000X. At these magnifications, the finish of virgin heads can be examined in detail. By the use of Nomarski interference microscopy, the presence of surface films are readily detected which provides a convenient means for examining the cleanliness of heads. The presence of hard and soft second phases in head materials (lead particles in leaded brass, and CuAl particles in aluminum, etc.) is readily detected. Uneven polishing of the heads, caused by relief polishing in which the softer head materials are worn away faster than the harder materials, can be detected. Detailed examinations of the adhesive bond line between the magnetic laminates and the copper shields revealed the presence of delaminations, incomplete bonding, etc. Virgin tapes are examined at high magnifications, primarily to provide a reference for evaluating examination results of tested tapes.

To study tape-head wear mechanisms, tested tapes and heads were examined in detail at high magnification. The wear debris can be studied, the preferred locations of the wear debris on the head can be determined, and its size, shape, color, etc., established. Nomarski interference microscopy makes possible a detailed study of the tape-binder film formed on the heads. The relative thickness of the deposits on the different head materials can be determined and the presence of wear tracks and other wear artifacts revealed. These studies are useful in establishing the mechanisms involved in the wear of heads and tapes as they move across one another. Tested tapes can be readily examined at high magnifications (up to 3000X); however, most of the useful information is obtained at magnifications of 1000X or less. Change in the tape surface texture is examined and the nature of wear particles on the tape studied in detail. The location of wear particles on the tape as related to the separate head materials can be studied. Figures 14 through 16 show photographs of tapes and heads illustrating some of the observations made at high magnifications.

The potential usefulness of the scanning electron microscope in examining magnetic tapes was evaluated on a limited and preliminary basis. Results of this evaluation were inconclusive principally because of the limited number of specimens examined and the inexperience of the microscope operator with techniques for examining magnetic tapes. Materials Research and Development personnel are presently engaged in gaining experience in using a recently procured scanning electron microscope. Emphasis will initially be on use of the microscope for evaluation of examination techniques for magnetic tapes. The scanning electron microscope has advantages over conventional light microscopes in the examination of magnetic tapes. Among these advantages are the following:

- Higher magnifications are available (useful magnifications of at least 20,000X to 30,000X).
- Resolution is superior at intermediate and high magnifications.

- Depth of field is much greater at high magnifications.
- Magnifications as low as 20X can be used for preliminary examinations with the capability of increasing the magnification incrementally to the maximum usable magnification.

Preparation of Tape Cross-Section Specimens. Attempts were made to develop methods for preparing cross-section specimens of magnetic tapes without altering their original condition. These specimens are required for determining the thickness of the tape binder and backing and for investigating the surface profile of the binder on virgin and worn tapes. The first step for evaluating cross-section specimen-preparation techniques was to establish the amount of binder distortion occurring during preparation of the cross-section specimens. A metal scribe and a razor blade were used to make artificial defects at known locations on several tape specimens. A variety of methods were used to mount and polish these specimens. Mounting methods investigated included clamping the tape specimens between aluminum, stainless-steel, or teflon clamps, or potting the tapes in epoxy or woods metal. Clamping the tape specimens between teflon clamps was judged the most satisfactory mounting method. Wet grinding on SiC papers was judged superior to dry grinding. Final polishing was done on kittens-ear cloth or silk, using 0.05μ Al_2O_3 power; silk produced the superior finish. To minimize cold flow and rounding of the tape edges, a minimum of time should be spent in final polishing. Examination of tapes purposely damaged showed that tape-binder flow was sufficient to obscure the defects, except where defects severely distorted the tape backing. Figure 17 shows one of the artificially created defects; tape binder has partially filled in the defect. This study showed that tape cross-section specimens are not useful for examining the surface profile of the tape binder. However, cross-section specimens of magnetic tapes can be used for determining the nominal thickness of tape binders and backings. Figure 18 presents photographs of tape cross-section specimens showing the relative thickness of the binder and mylar backing on two grades of tape. The preferred metallographic technique discussed in the foregoing was used in preparing the specimens from which these photomicrographs were obtained.

Head-Tape Compatibility Tests

It was observed that as a function of the construction materials, a film forms on certain areas of tape-recorder heads during recorder operation. This suggests that certain head materials may be incompatible with some tape binders. To investigate the compatibility of magnetic head and tape materials, a special test was designed in which magnetic tapes were placed in contact with various head materials under selected loads and temperatures. Figure 19 shows the test arrangement and a film formed on brass test heads which were in contact

with 3-M 551 tape at 150° F for 3 days. Aluminum heads exposed under the same conditions showed no film. It was determined that the film was caused by an organic dye present on the oxide surface of the tape. The foregoing test arrangement is a convenient method for investigating the compatibility of tapes and heads under a variety of environments.*

Blocking Tests

The blocking test is an accepted evaluation test method (Fed. Std. Test Method 1131) for determining the tendency of films, papers, tapes, etc., to adhere to themselves. It was considered that the temperature at which blocking occurs would be a criteria for evaluating the relative tendency of magnetic tapes to stick to the heads. The following blocking tests were conducted on samples of RCA 617 tape.

Two sections of tape, 3 inches long, were placed with their oxide surface face to face with a 1-inch length of the tapes in contact. The two sections of tape were placed between two glass slides supported on a metal plate, and a 2-pound weight placed on the top glass slide. The test assembly was then placed in an 125° F oven for at least 12 hours. The assembly was removed from the oven and allowed to cool to ambient temperature, and the degree of bonding or sticking of the two sections of tape was observed. Six samples of RCA 617 tape were tested in this manner; in none of the samples was any bonding or sticking observed. The tests were repeated at 150° F, with the same results.

Mechanical Tests

Tensile Tests. Tensile tests are principally used to evaluate the mechanical properties of magnetic-tape substrates. For tapes with mylar substrates, the tensile test also provides information on the degree of orientation and crystallinity of the mylar. Data from tensile tests are useful in evaluating the effect of environmental parameters on magnetic tapes (samples of 3-M 617 and RCA 551 magnetic tapes were irradiated with a cobalt 60 source to obtain samples with a range of adsorbed doses from 10^5 rads to 10^8 rads). Results of tensile tests conducted on these irradiated tapes showed that exposure to 10^8 rads appreciably lowered the ductility of the mylar substrate, embrittled the binder, and damaged the adhesion of the binder to the mylar substrate. In Figure 20, the tape binder is almost gone from the 10^8 rad specimens of 617 and 551 tapes. The binders on the remaining irradiated and virgin tape specimens are nearly intact. The reduction in cross-sectional area of the 10^8 rad tensile specimens is much smaller than the reduction on the other irradiated specimens.

*A more detailed discussion and analysis of the observed metal-head film is presented in an earlier section of this report.

Hardness Tests. Preliminary hardness tests have been conducted on samples of RCA 551 tapes using a Reichert microhardness tester with a diamond pyramid indenter and a 1-gm load. In these tests, reproducibility and accuracy were poor principally for the following reasons:

- Load control is difficult: 1 gm, the lowest load provided, is difficult to reproduce exactly from test to test.
- Hardness impressions obtained were indistinct and difficult to measure. To improve the contrast of the impressions, tape specimens were coated with a thin vapor deposit of aluminum approximately 1000 Å thick. Test results were negative.
- The shape of the impressions obtained indicates that a very large elastic recovery of the impression occurs when the load is removed. This accounts in part for the difficulty of measuring the impressions and for the inaccuracy of the hardness values obtained.

Even though the hardness-test results have been negative to date, microhardness techniques will be examined further, because the hardness of the tape binders as a function of temperature would be an extremely useful piece of information.

Surface-Roughness Measurement. Measurement of the surface roughness of virgin magnetic tapes provides an index for comparison with surface-roughness measurements made on tested tapes. The difference in the surface roughness of virgin and tested tapes may provide information on the degree of tape wear and the location of severely worn areas and areas with redeposited wear debris. Preliminary surface-roughness measurements were made with a Talysurf Profilometer; samples of 11 different tapes were tested. Results of these tests show that the tapes generally exhibit a long-range coarse, undulating surface roughness with a superimposed short-range fine surface roughness. Table 2 lists some results of tests on virgin tapes. Figure 21 shows a typical Talysurf trace.

ELECTRON MICROSCOPE, X-RAY, AND OTHER ANALYTICAL PROCEDURES FOR THE INVESTIGATION OF MAGNETIC TAPE

Various examination techniques have been used to characterize the inorganic components of magnetic recording tapes. The spatial relationship of these inorganics in an organic matrix has been observed. These studies were done to determine what tape characteristics were measurable or descriptive, and whether these might be used to indicate a change in tape performance.

X-Ray Diffraction Analysis

X-ray identification of the composition of oxide used on the tapes is complicated by the similarity of the x-ray diffraction patterns for the two magnetic oxide phases commonly used: $\gamma\text{-Fe}_2\text{O}_3$ (Maghemite) and Fe_3O_4 (Magnetite) (Table 3). Information from a tape oxide manufacturer and the electron microprobe analyzer establishes the active element in the tapes as $\gamma\text{-Fe}_2\text{O}_3$. Differences in the color of the oxide pigments in many cases indicate a graphite/iron oxide mixture and not a change in ferric-oxide stoichiometry.

Electron-Diffraction Analysis

Electron-diffraction analysis was used to identify other crystalline compounds in the organic binders. Figure 22 shows a micrograph of a conglomerate of graphite platelets separated from tape 617 and an electron diffractogram characteristic of a graphite structure.

Electron Microscopy

The morphology and size distribution of the active element ($\gamma\text{Fe}_2\text{O}_3$) in the binder layer can be characterized in three ways:

- Tape replication—to determine the surface structure of the oxide-binder layer (Figures 23 and 24)
- Tape cross-sectioning (Figure 25)
- Separation of oxide particles, followed directly by particle viewing in the electron microscope (Figure 26)

These techniques have been successful in determining the uniformity of oxide-particle shape and size distribution within the binder matrix and the structure that the particles induce (Table 4).

Six tapes were replicated, and micrographs representing the surface textures observed (Figure 23) were obtained.

Thin sections of tape 617, obtained by ultramicrotomy, were viewed directly through the electron microscope. Figure 25, a typical micrograph of one of the thin sections, shows smearing and tearing of the binder. The oxide particles are randomly and homogeneously distributed.

Preferred Orientation

X-ray pole figure analysis and microscopy were used to determine the existence of texture or preferred orientation. The data from the tapes examined showed no indication of preferred orientation.

Emission Spectroscopy

This has always been a sensitive technique used in searches for minor elemental constituents. The method has detected the presence of silicon which may indicate that silicone lubricants are part of the binder. For example, in an emission spectrographic examination of RCA tape 617, a spectrum was obtained of magnetic oxide free from all polymers and a subsequent spectrum was made of the combined binder and oxide. The second spectrographic examination revealed a hundred-fold increase in the silicon content. This confirmed previous IR analysis of tape 617 extractions which indicated the presence of silicone lubricants. Table 5 shows the comparative elemental analysis of the γ Fe_2O_3 and Fe_3O_4 with polymer binder.

RECOMMENDATIONS

Additional areas of test suitability still have to be probed. These should include the following:

- Determine binder-film moisture sensitivity, as a function of surface resistivity in various environments.
- Develop a thin-layer chromatography analytic system specifically to identify small amounts of tape-binder additives.
- Develop qualitative or quantitative techniques for determining the adhesion of binder to particle or binder to carrier.
- Develop a catalog of infrared-pyrolysis fingerprints for available types of polyurethane resins and additives.

CONCLUSION

Differentiating analytical techniques are available for identifying tape carriers or backing. Urethane chemistry is exceedingly complex, and only general differentiation can be made between various urethane binders; however, binders outside this class can be easily identified.

The mechanics of detailed analysis for small quantities of binder additives have not yet been worked out. The usefulness of many optical and metallurgical techniques have been proved. The recently acquired scanning electron microscope should be useful in developing adhesion criteria.

SOURCES

The following Materials Research and Development Branch personnel developed the experimental information for this document:

- Polymer Chemistry Section — Edward Nelson, Frederick Gross, Benjamin Mermelstein, Carroll Clatterbuck, George Biddison
- Metals Section — Jane Jellison, William Latham
- Ceramics Section — Thomas Heslin
- Electronic Materials Section — Peter Sarmiento, Richard Marriot

REFERENCES

1. Green, C. V. "Chemical Analysis of Magnetic Recording Tape." Journal of the Audio Engineering Society. Vol. VIII, 3. July 1960.
2. Grimsley, John and James Jarrett. "Designs and Construction of a Magnetic-Tape Testing Machine." NASA Technical Note.

PRECEDING PAGE BLANK NOT FILMED.

APPENDIX A

INTERIM REPORT ON CHEMICAL CHARACTERIZATION OF 3-M 551 MAGNETIC TAPE

Materials Research and Development Branch,
Polymer Section

This report describes the chemical characterization of 3-M 551 magnetic-tape binder, which was found to be the normal type of polyester-based polyurethane elastomer. The polyurethane binder is assumed to be thermosetting because no solvent was found to soften it. This analysis emphasized binder composition and the extracts obtained from the tape.

An unsuccessful attempt was made to run an infrared spectrum of the surface by attenuated total reflectance. Organic binder coverage of the iron-oxide filter in the binder of 551 tape appears to be insufficient to give a spectra under the test conditions. However, an attenuated total-reflectance spectrum was run on the non-binder side of the tape. The tape carrier was shown to be composed of polyethylene terephthalate.

An infrared spectrum run on the pyrolyzate of the 551 binder shows a pattern similar to those obtained in pyrolysis of polyester-based polyurethanes and to the spectra obtained in earlier work on a series of RCA tapes. The pyrolysis spectra showed the presence of aromatic groups, amines and/or amides, strong ester absorption, and possibly hydroxyl groups.

A series of solvent extractions with benzene, chloroform, and ethanol run on the 551 tape showed that results of the benzene and chloroform extractions were similar. Infrared spectra of the residues from these two extractions showed the presence of an aliphatic long-chain ester. The residues were colored red by dye or pigment. This dye or pigment was concentrated through extraction of the chloroform extract residue with aqueous ethanol. The dye was soluble in ethanol in both basic and neutral solutions but precipitated by acid. The dye has an absorption at $555\text{ m}\mu$ in a basic solution and a $558\text{ m}\mu$ in a neutral one. It also has a strong visible fluorescence. The dye appears to be similar to Rhodamine B and may be included primarily to indicate good magnetic coating coverage of the web during tape fabrication.

The residue of part of the ethanol extract gave a spectra of a rather impure ester with hydroxyl groups present. The rest of the extract was made basic with potassium carbonate, evaporated to dryness, and extracted with acetone.

The acetone wash after acetone evaporation gave an infrared spectra of hydroxyl, aliphatic carbon hydrogen, esters, possible ethers, and long chain methylenes.

The potassium-carbonate residue was washed with acetone, then acidified with hydrochloric acid, and extracted with chloroform. The infrared showed the presence of fatty acid after the chloroform evaporated.

The 3-M 551 tape is polyethylene terephthalate-backed magnetic tape with the organic fraction of the magnetic layer, an ester-based polyurethane resin which contains some unreacted esters, fatty acid, and a dye or pigment similar to Rhodamine B. This tape showed no signs of silicone fraction.

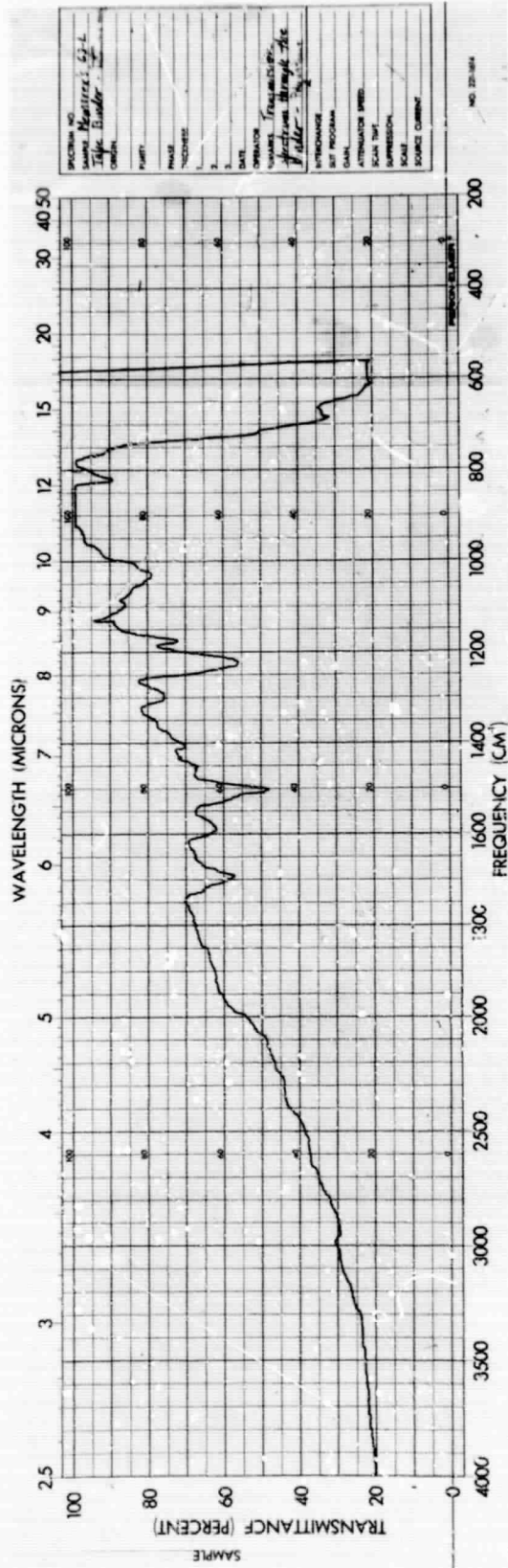
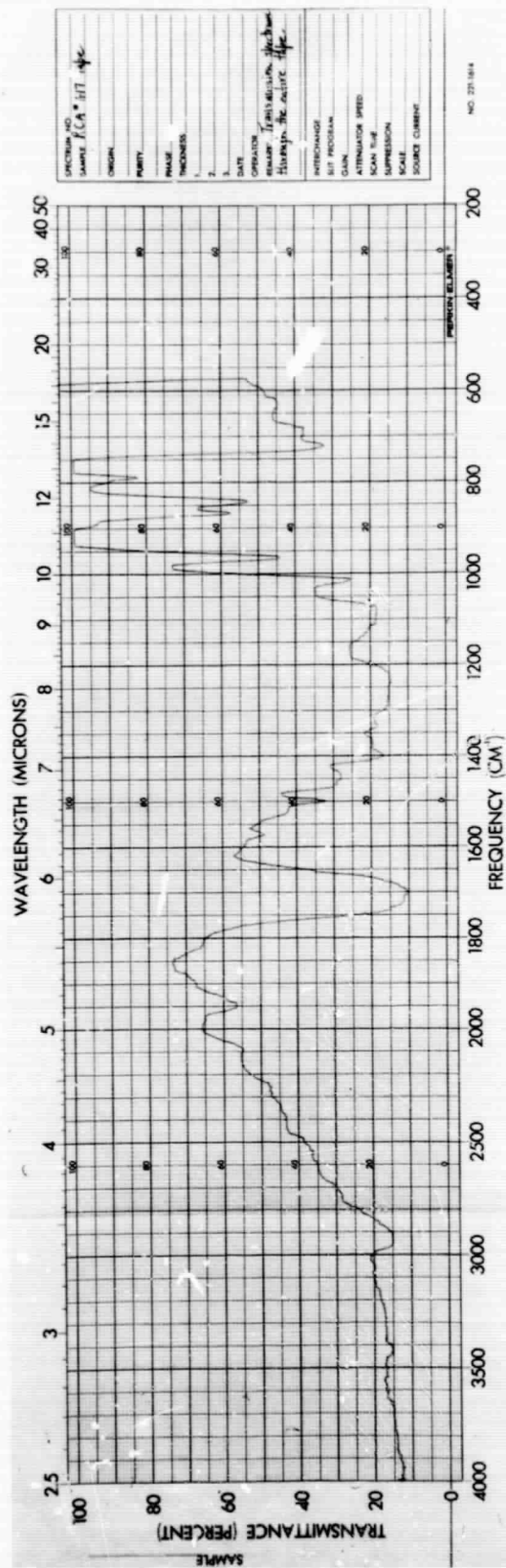


Figure 1. Typical Infrared Traces of Complete RCA Tape 617 and Binder Separated from Memorex 62-2

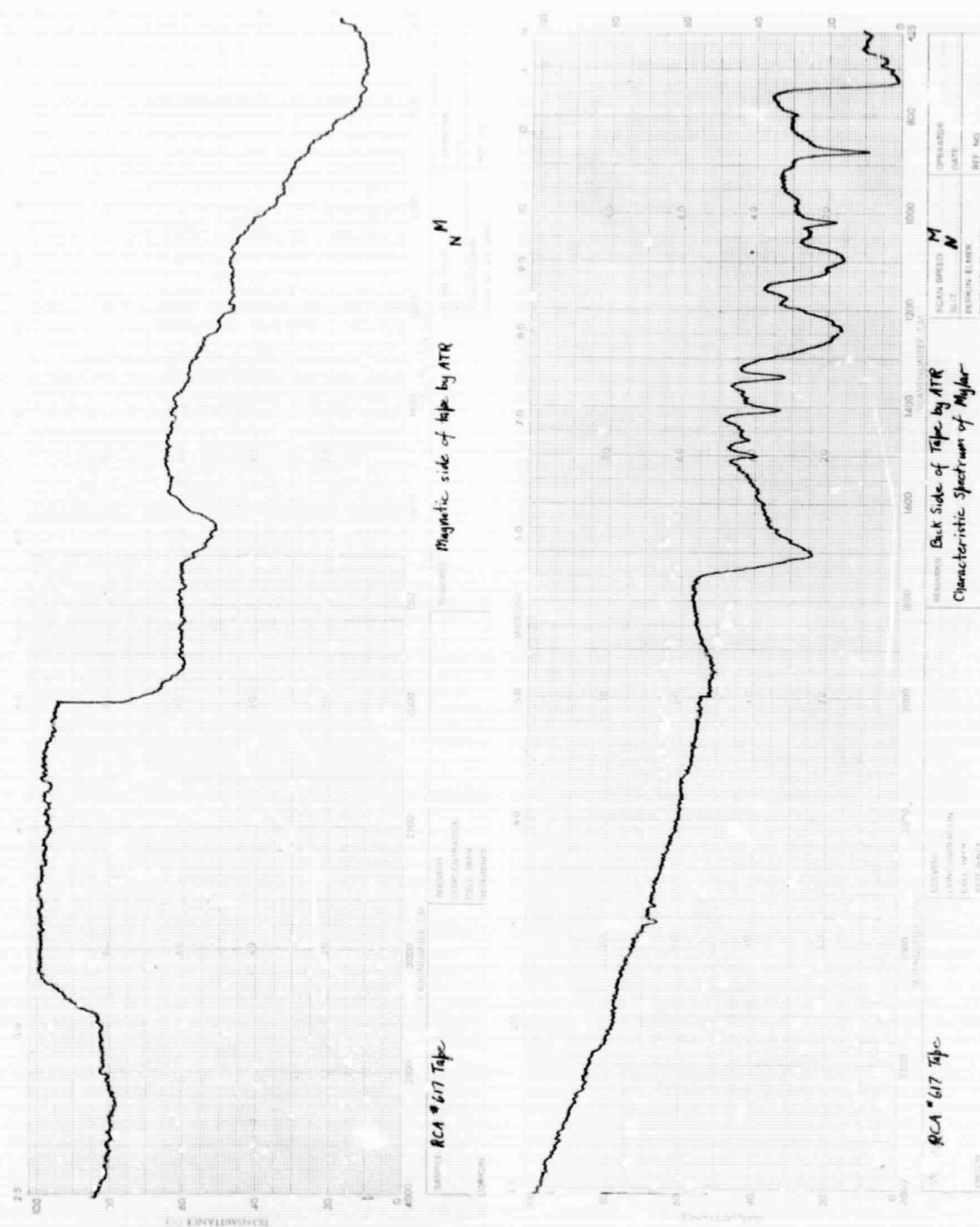


Figure 2. Typical ATR Spectrum of Mylar Tape, Front and Back

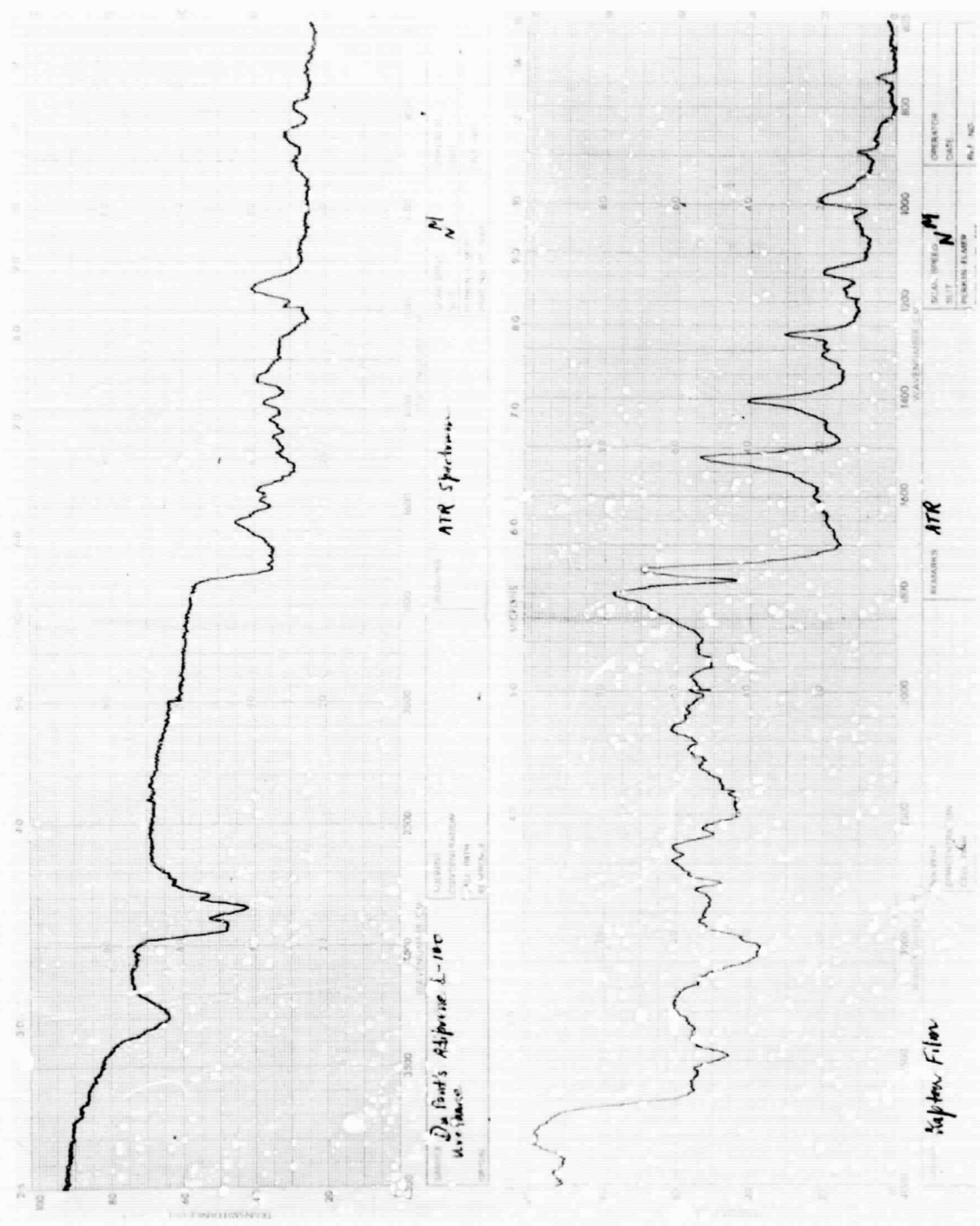


Figure 3. Comparative ATR Spectra of Cured Polyurethane and Kapton Film

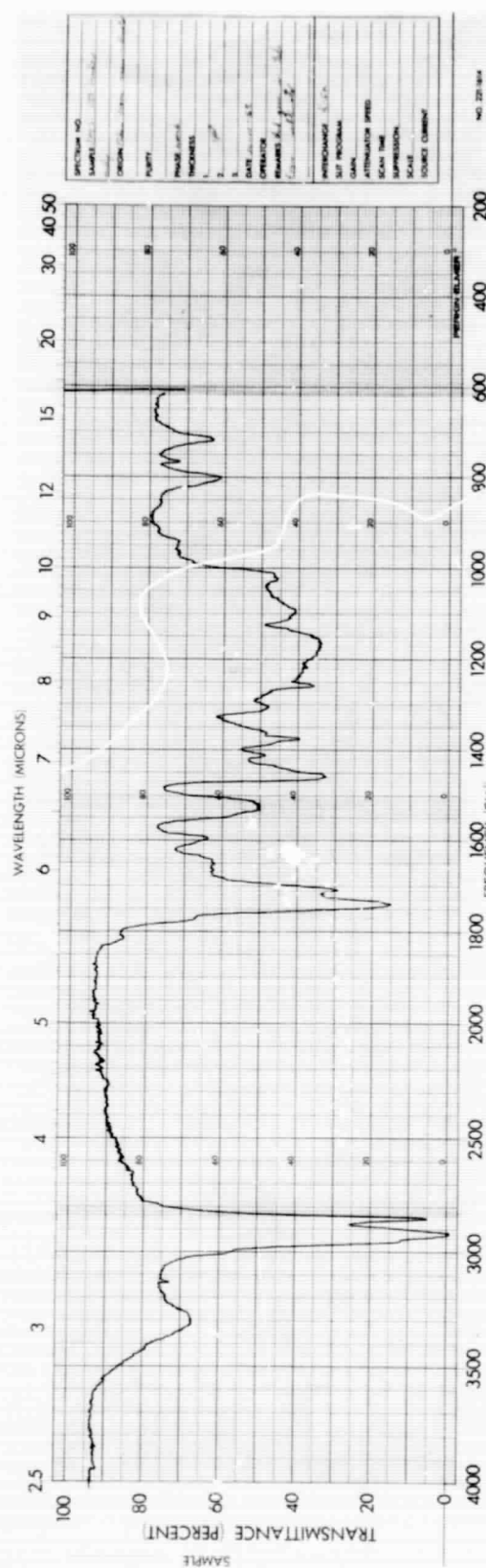
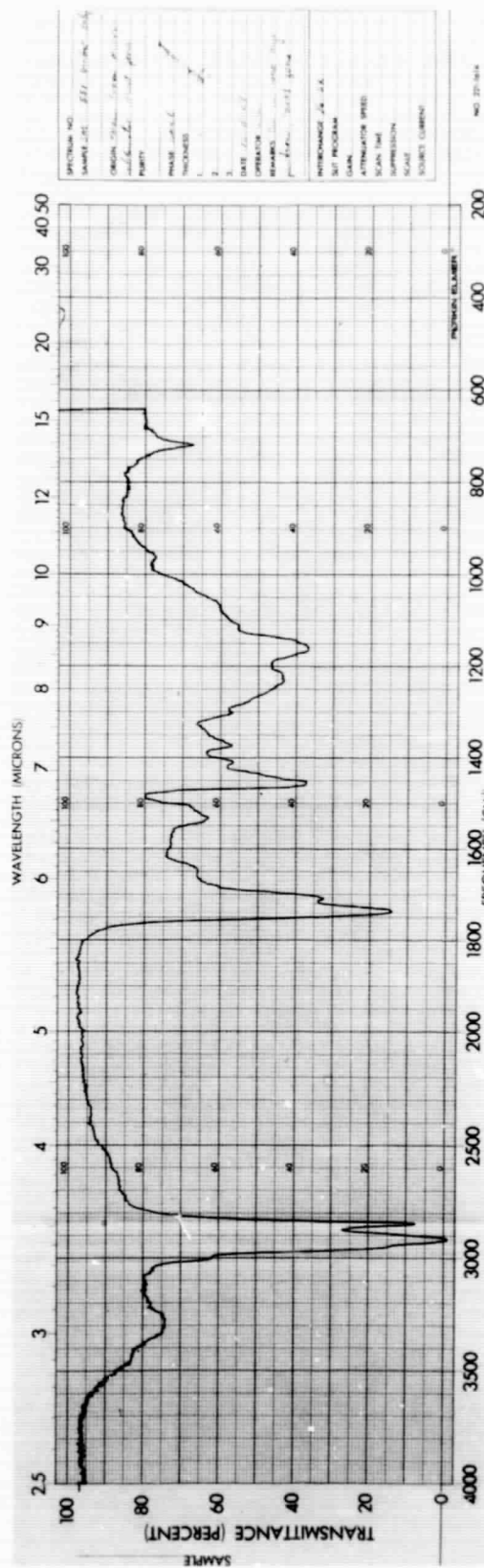
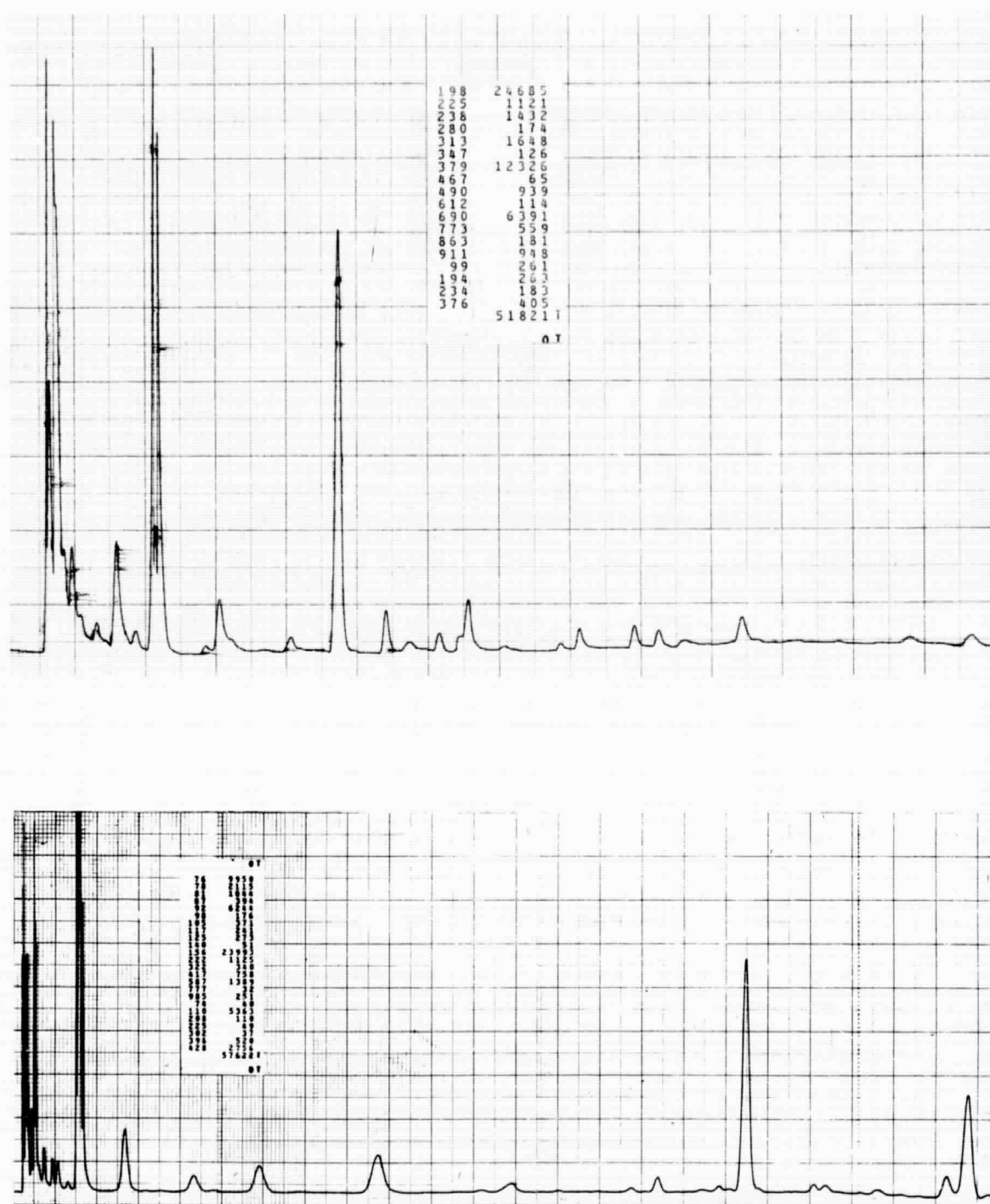
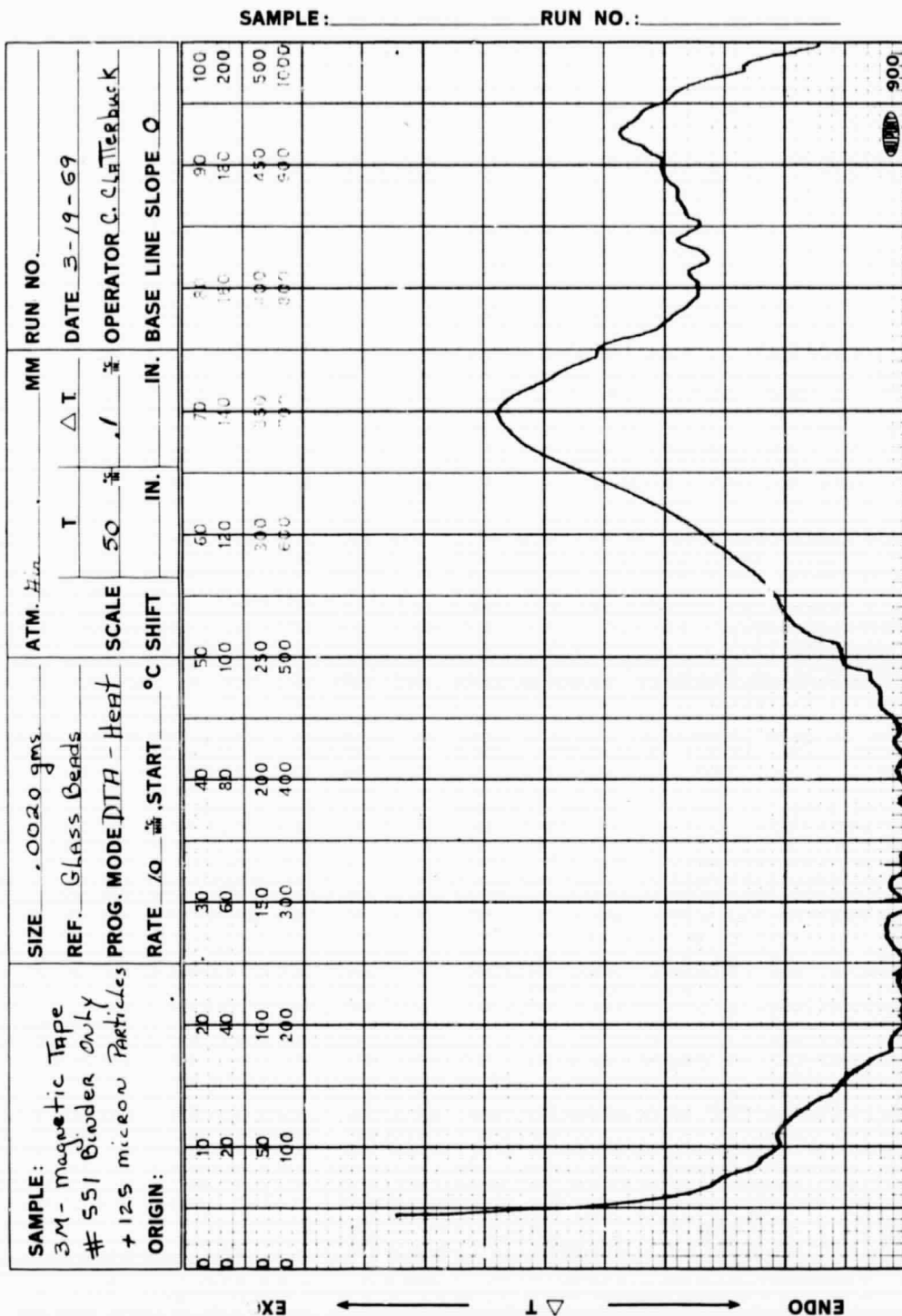


Figure 5. Infrared Spectra of 3-M 551 Tape Binder, Vacuum Heated and Vapors Condensed in a Thermal-Gradient Tube



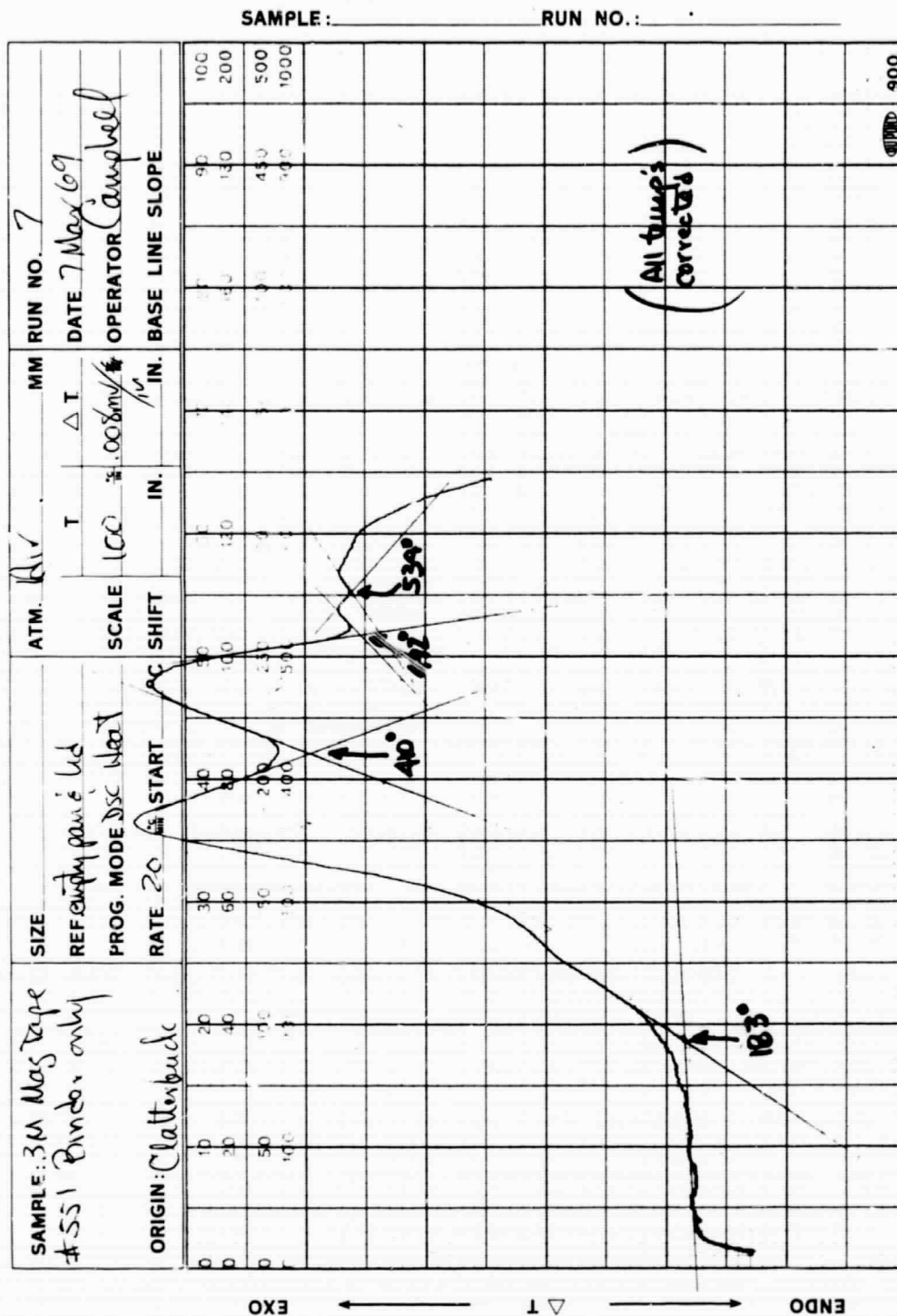
PART NO. 900304



* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

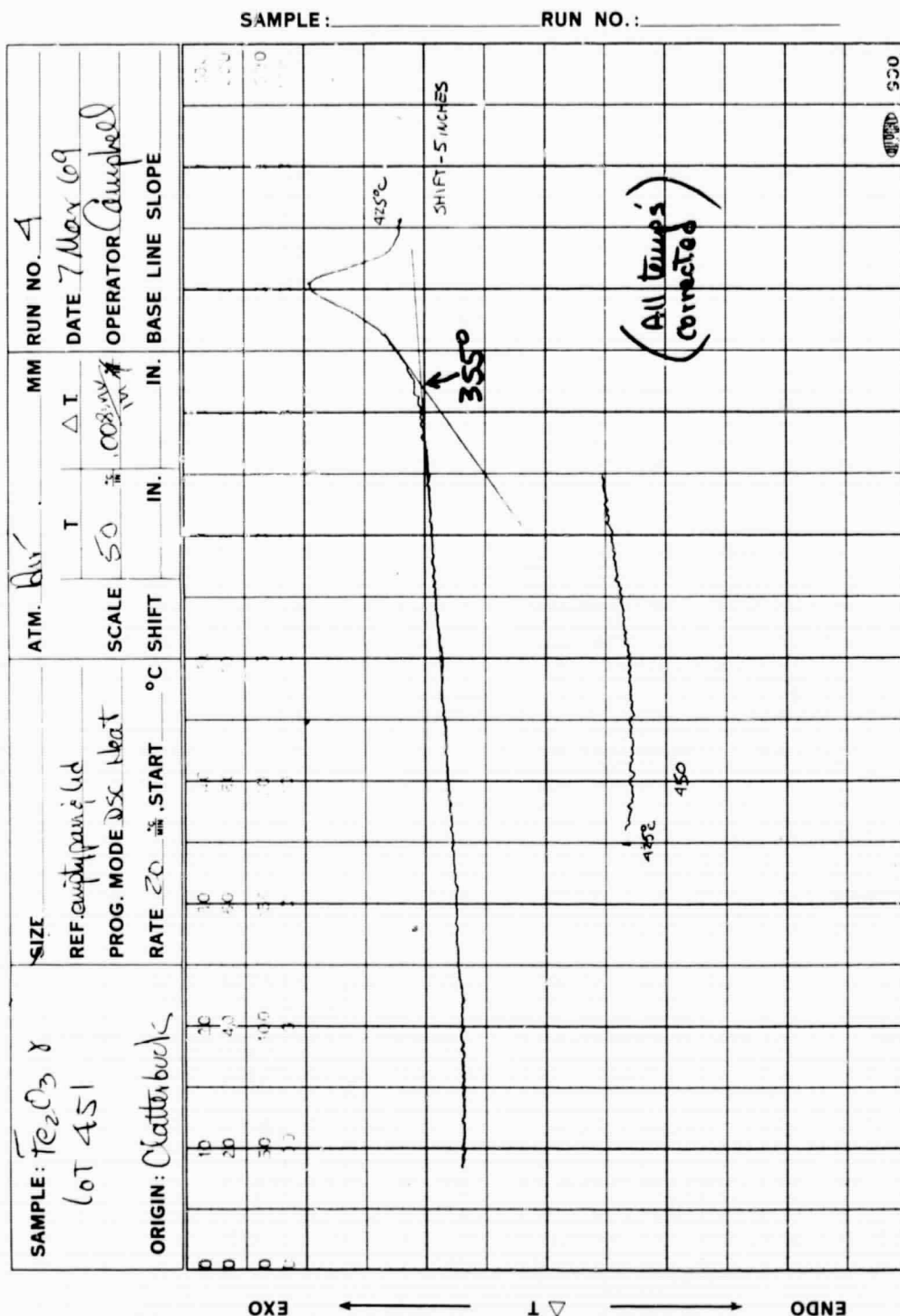
T, °C (CHROMEL: ALUMEL)*

Figure 8. Differential Thermal Analysis Trace of 3-M 551 Binder



T, °C (CHROMEL: ALUMEL) * SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

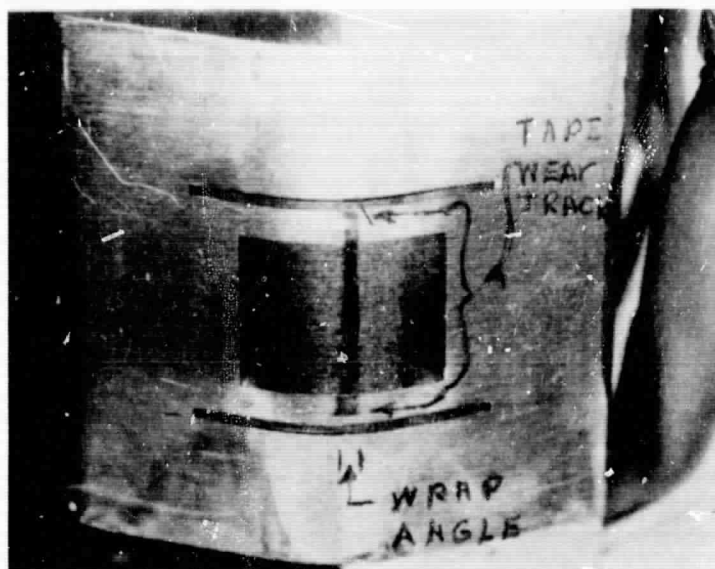
Figure 9. Differential Scanning Calorimeter Trace of 3-M 551 Binder



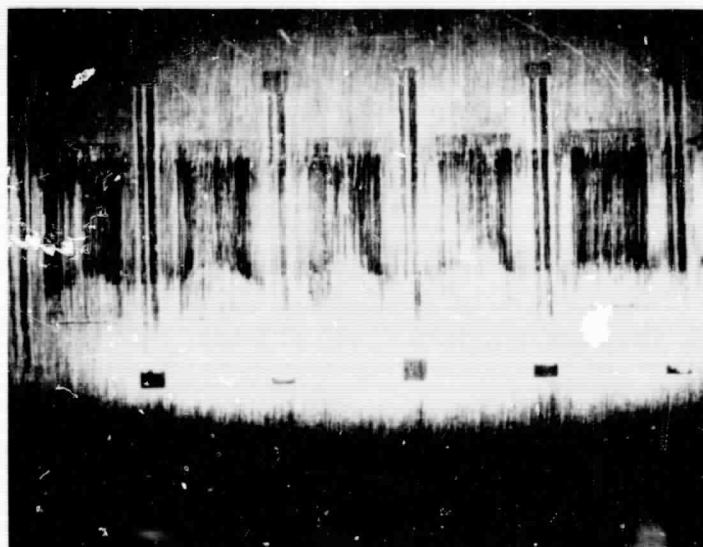
* SEE INSTRUCTION MANUAL FOR SCALE CORRECTION

T, °C (CHROMEL: ALUMEL)[®]

Figure 10. Differential Scanning Calorimeter Trace of γ Fe₂O₃

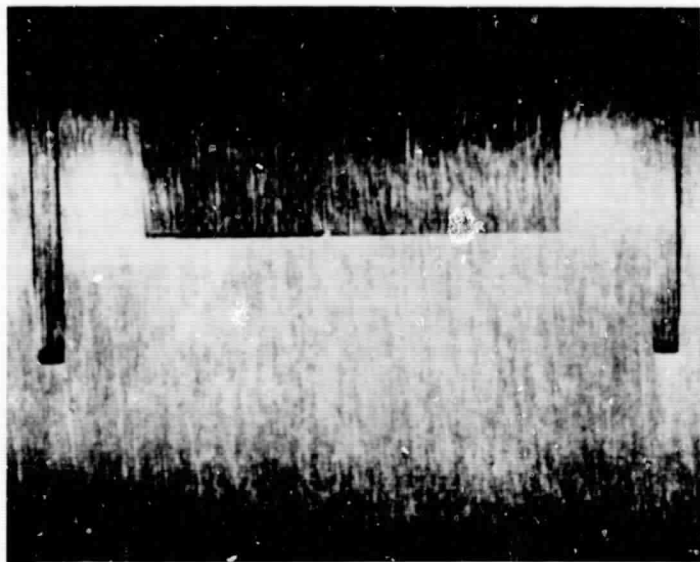


a. OSO Aluminum Recorder Head
(3 x Magnification)



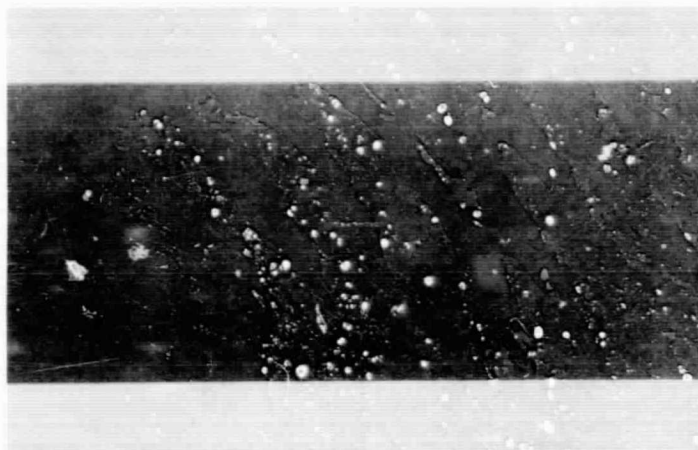
b. Brass Recorder Head After Test on
Continuous Loop Machine (6 x Magnification)

Figure 11. Low-Magnification Appearance of
Tape-Recorder Heads After Use

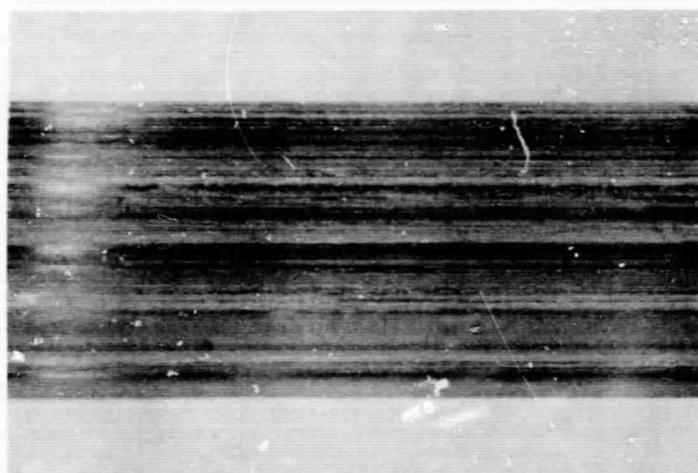


(6 x Magnification)

Figure 12. Photograph of As-Polished Tape-Recorder Head Showing Voids in Potting Material and Surface Finish of Head

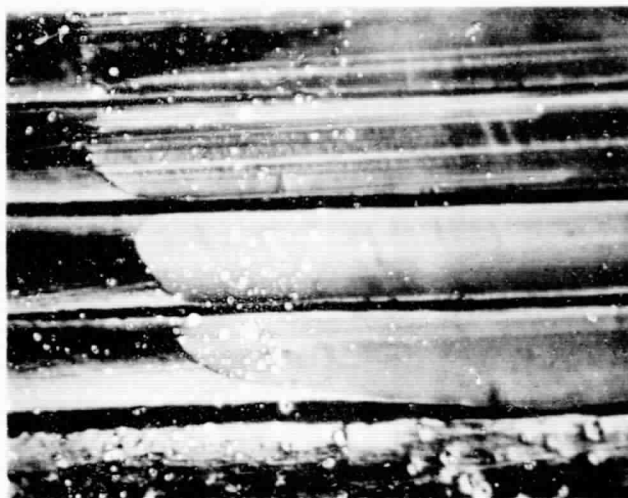


a. Before Test (3 x Magnification)



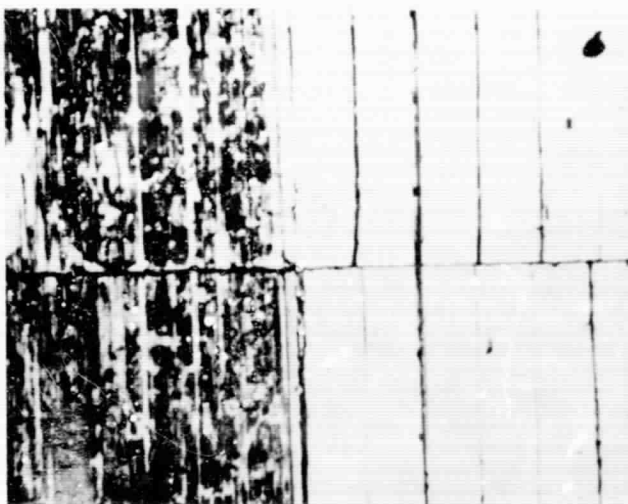
b. After 17,000 Cycles (3 x Magnification)

Figure 13. Photographs of 3-M 551 Magnetic Tape, Before and After Being Run 17,000 Cycles Over Brass Recorder Heads on a Continuous-Loop Tape Machine



(250 x Magnification)

a. Wear on Mu-metal After 17,000 Passes of 551 Tape (Mu-metal Laminate Rounding Occurred During Polishing of the Head)

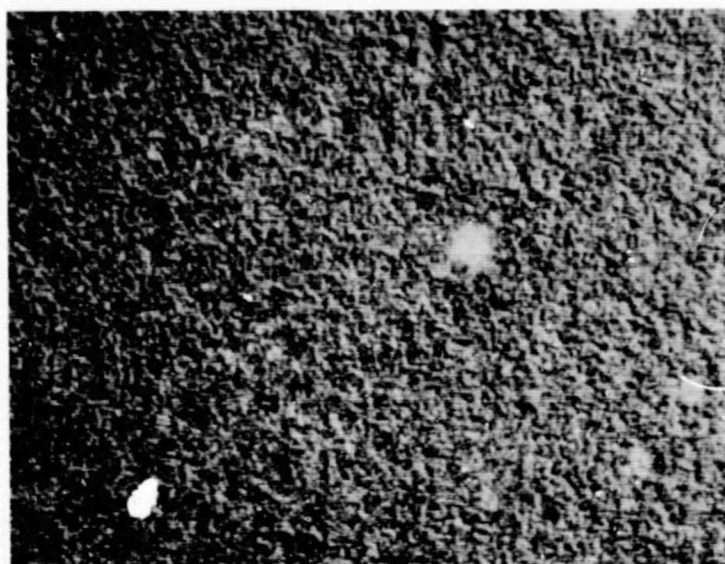


← Brass → | ← Mu-metal →

(100 x Magnification)

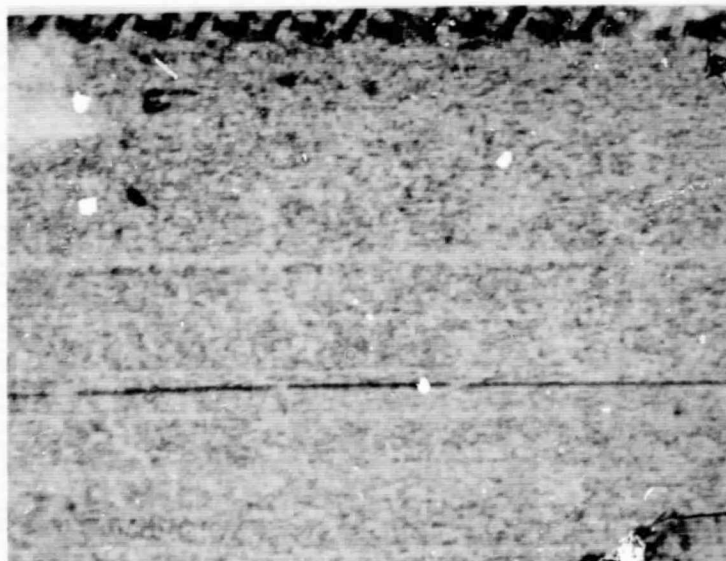
b. Film Formed on Brass Head After 40,000 Passes of 551 Tape (Note Lack of Film Formation on the Mu-metal)

Figure 14. Appearance of Brass Magnetic Recorder Heads After Use with 3-M 551 Tape



(250 x Magnification)

a. Virgin Condition



Wear track from
hard particle

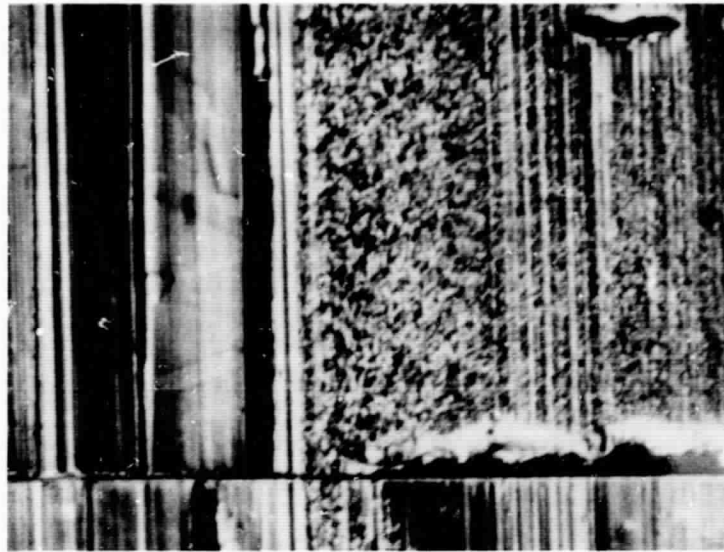
Scratch

Wear debris

(250 x Magnification)

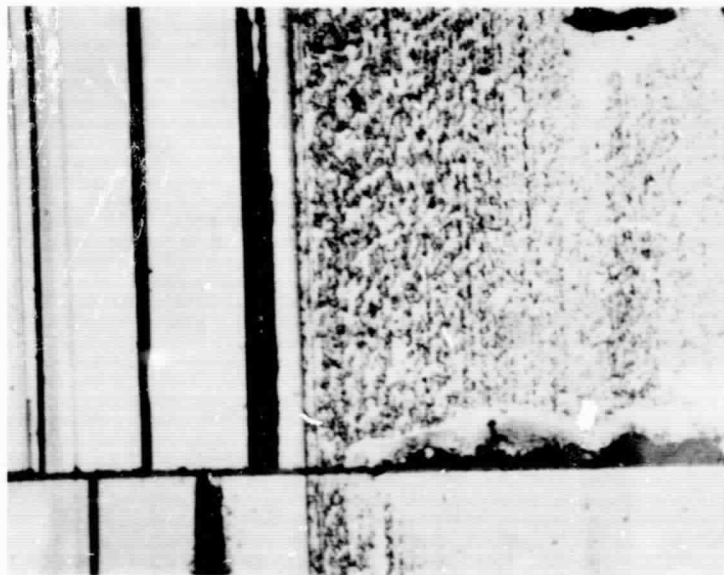
b. After 17,000 Cycles on a Continuous-Loop
Tape Machine

Figure 15. Appearance of 3-M 551 Tape, Tape in
Virgin Condition, and Tape After Run of 17,000
Cycles on a Continuous-Loop Tape Machine



(250 x Magnification)

a. Relief Polishing From Tape Shown by Nomarski Interference Illumination

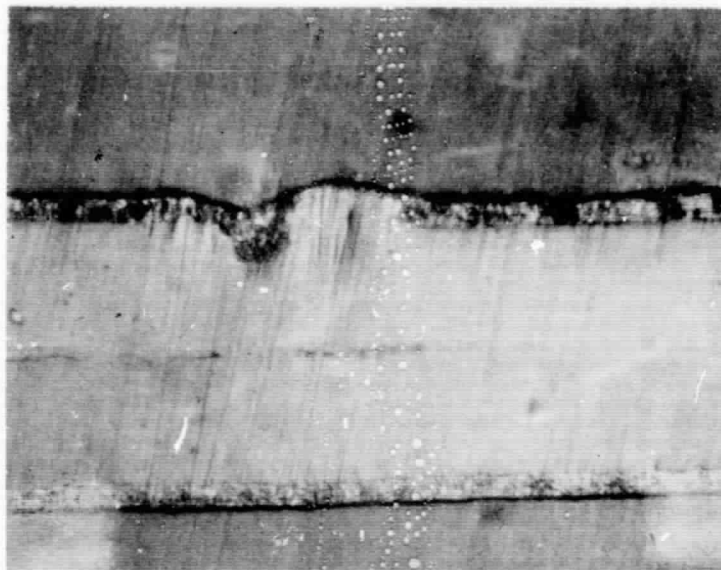


← Mu-metal → | ← Brass →

(250 x Magnification)

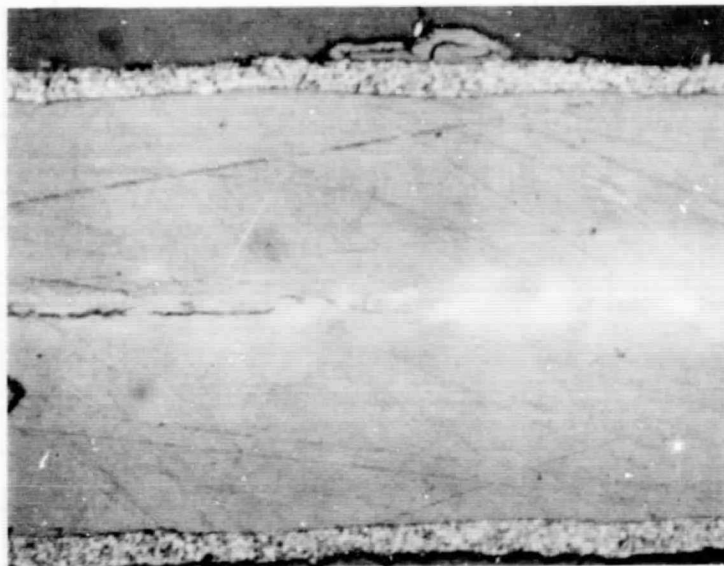
b. Bright Field Illumination

Figure 16. Brass Magnetic Head After Test With 3-M 551 Tape



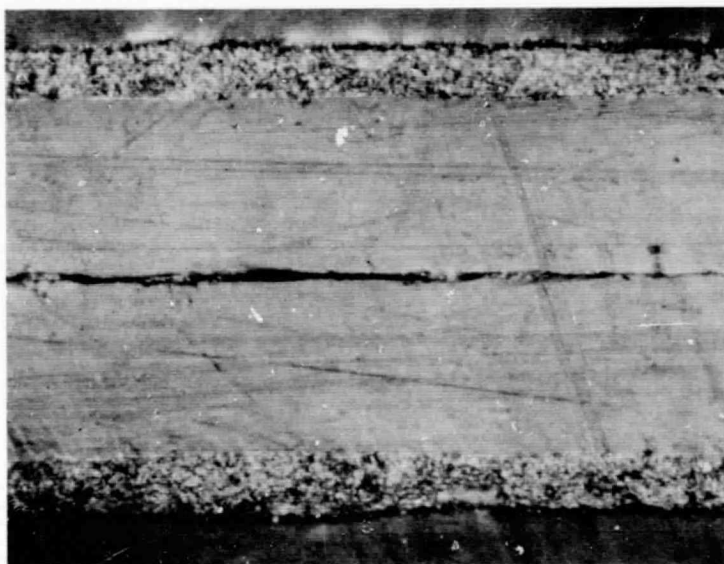
(750 x Magnification)

Figure 17. Cross-Section of 3-M 551 Tape Showing Artificial Defect Made with a Steel Scribe



(1000 x Magnification)

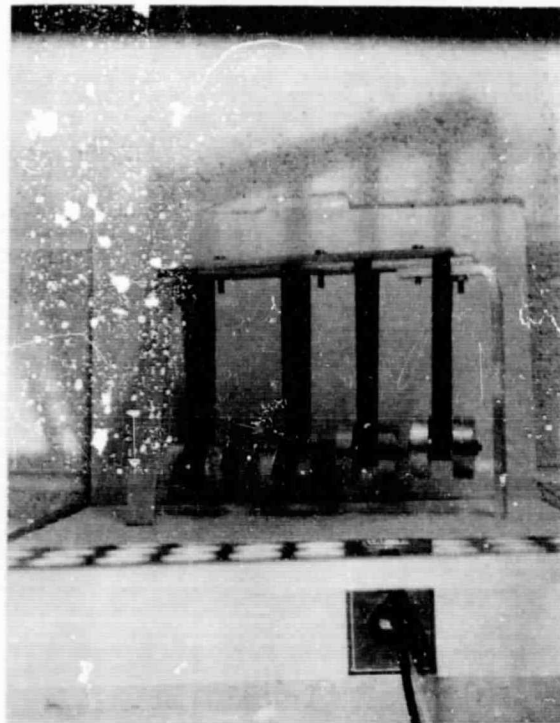
a. Cross-Section of 3-M 551 Tape



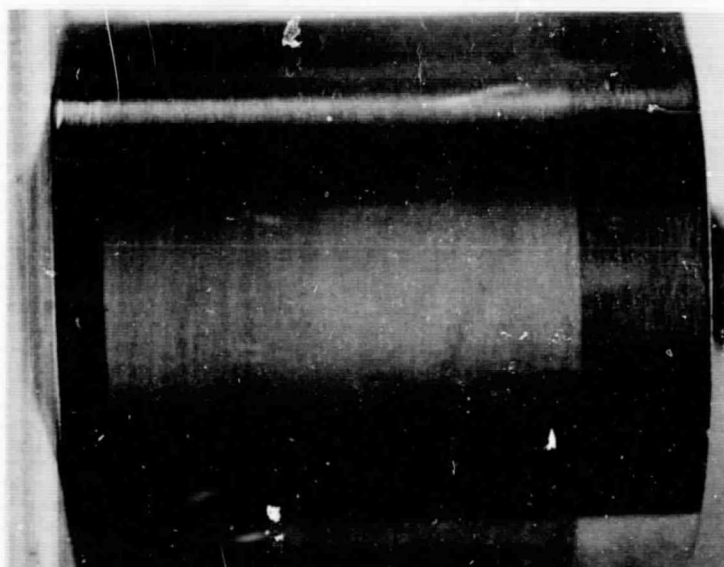
(1000 x Magnification)

b. Cross-Section of RCA 617 Tape

Figure 18. Cross-Section Specimens of Magnetic Tapes

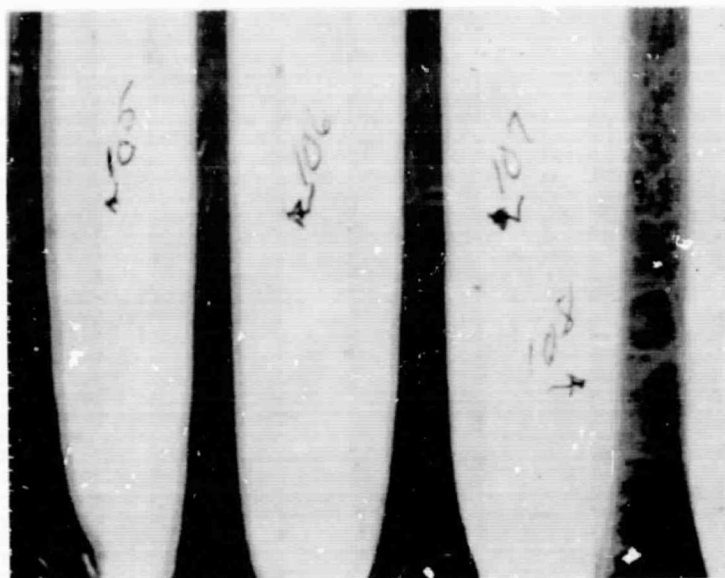


a. Head/Tape Compatibility
Test Arrangement



b. Brass Head After Compatibility Test (3 Days at
150°F in Contact with 3-M 551 Tape)

Figure 19. Head/Tape Compatibility Tests



(1.4 x Magnification)

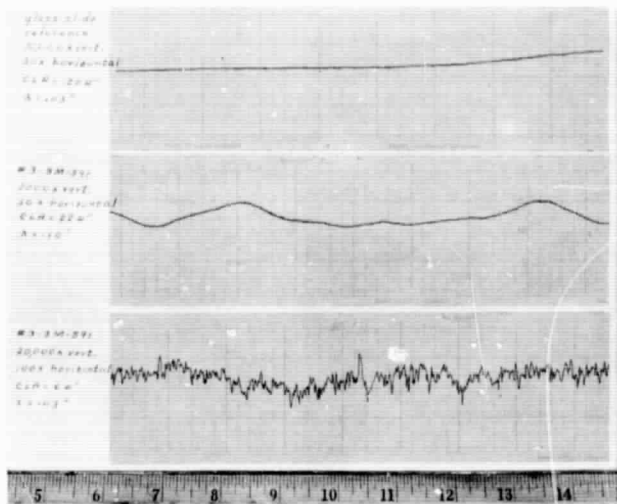
a. RCA 617 Tape



(1.4 x Magnification)

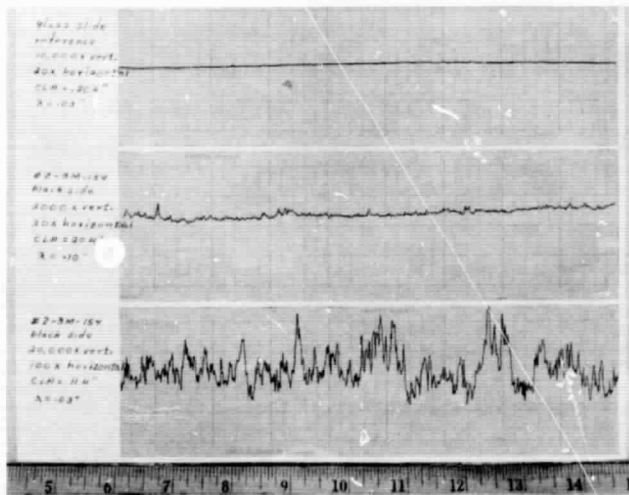
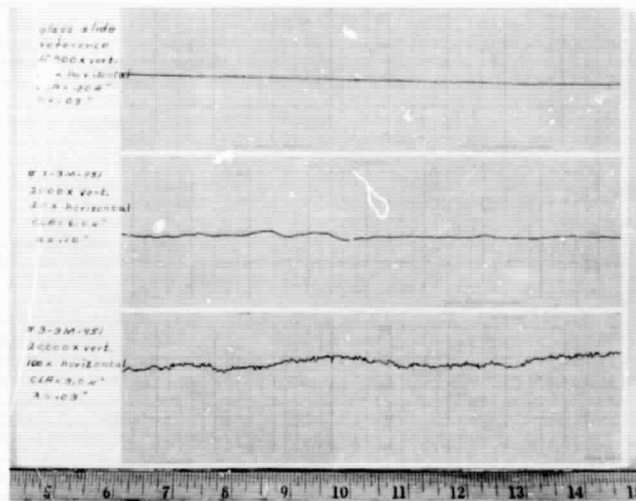
b. 3-M 551 Tape

Figure 20. Photographs of Irradiated RCA 617 and 3-M 551 Tape Tensile Test Specimens After Being Tested



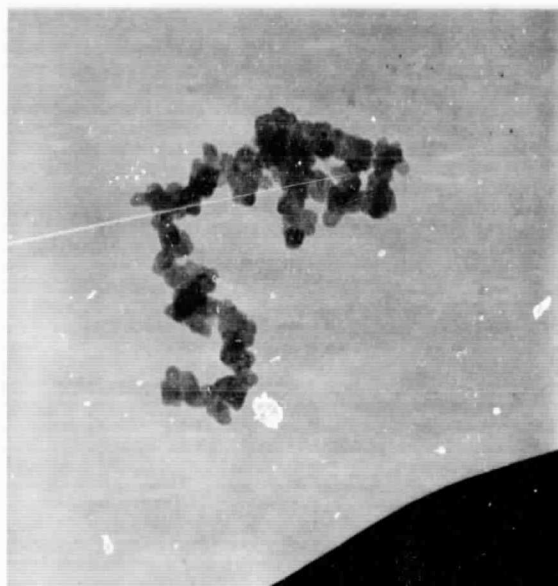
a. Profiles Showing a Surface with Two Distinct Textures

b. Profiles Showing a Surface with Two Textures (One of Them, a Coarse Texture, Is Not Very Pronounced)

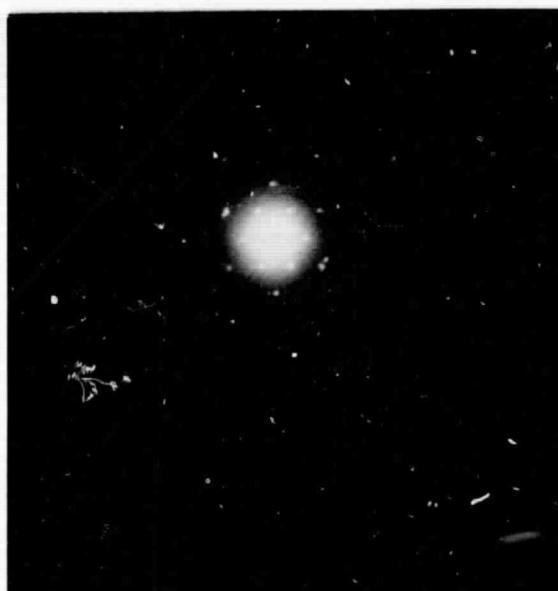


c. Profiles Showing a Surface with Essentially One Texture

Figure 21. Representative Tape Smoothness Profiles

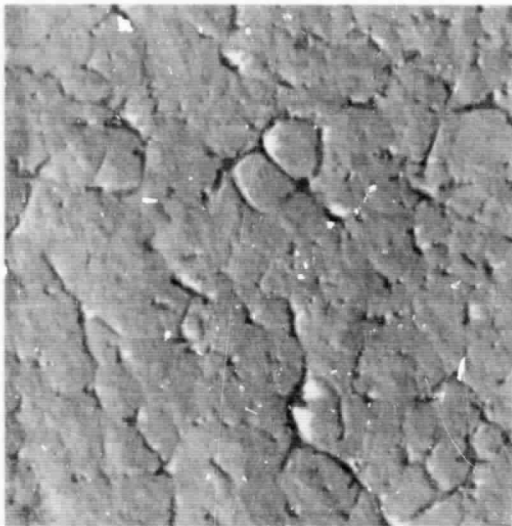


a. Electron Micrograph of Graphite Particles

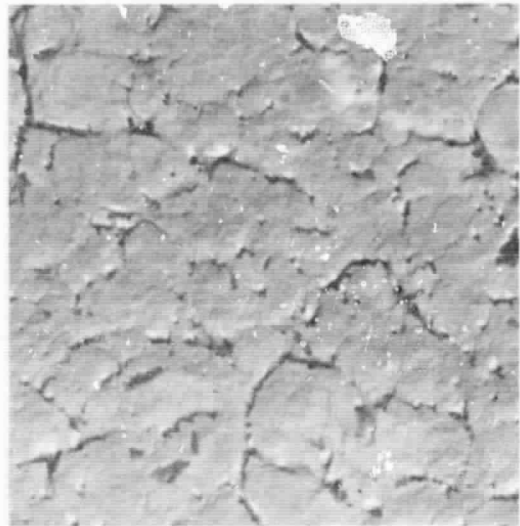


b. Electron Diffraction of Particles Shown in 7a

Figure 22. Graphite Particles Extracted From RCA 617 Tape



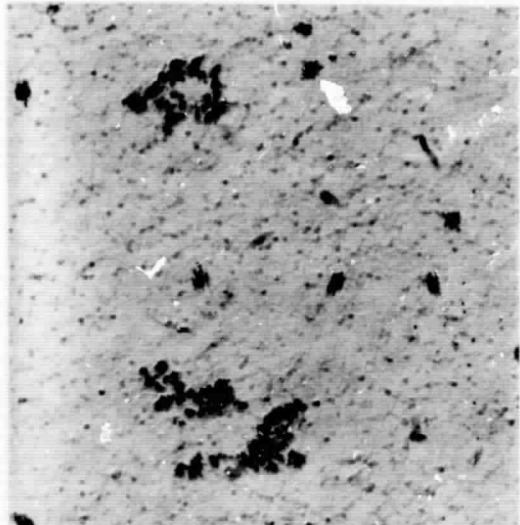
a. Tape 606C (10,000 x Magnification)



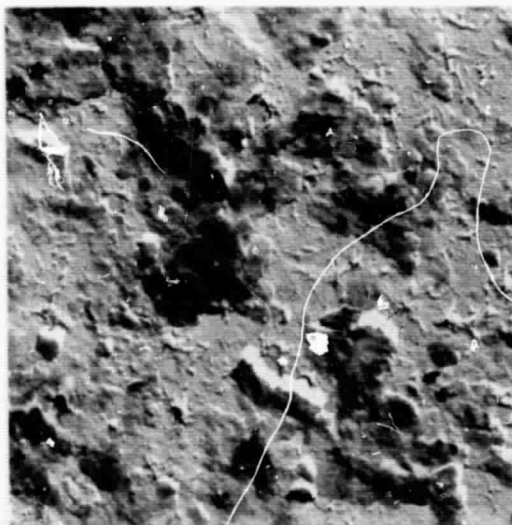
b. Tape 583C (10,000 x Magnification)



c. Tape 617 (8,000 x Magnification)



d. Tape 551 (1A6) (10,000 x Magnification)



e. Tape 551 (1A8) (10,000 x Magnification)



f. Tape 551 (1A2) (10,000 x Magnification)

Figure 23. Replicas of Tapes at Various Magnifications

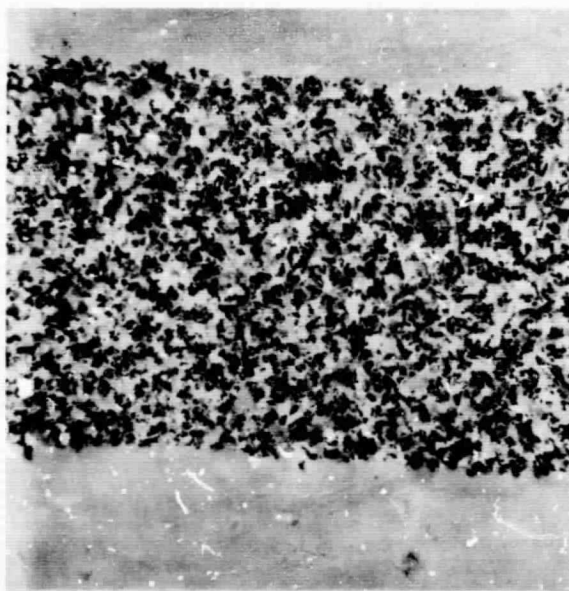


(10,000 x Magnification)



(10,000 x Magnification)

Figure 24. Examples of Surface Defects in RCA 617 Tape



(~ 5000 x Magnification)

Figure 25. Thin Section of RCA 617
Tape as Received



a. Tape 583C (30,000 x Magnification)



b. Tape 591GKI (30,000 x Magnification)



c. Tape 591V (30,000 x Magnification)



d. Tape 593B (30,000 x Magnification)

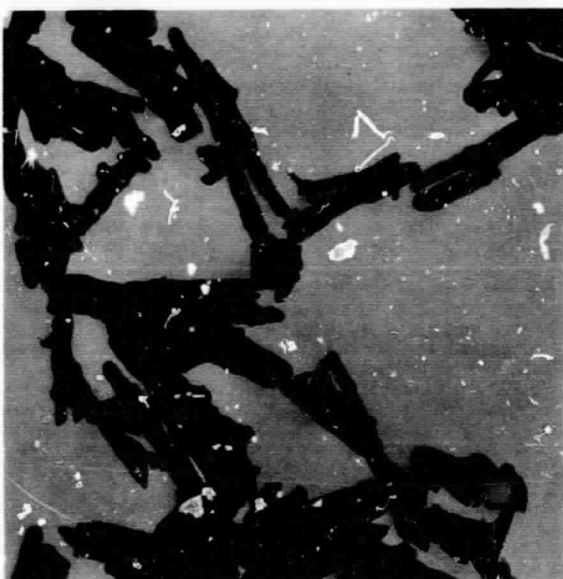
Figure 26. Particles Extracted from Various Tapes (Sheet 1 of 3)



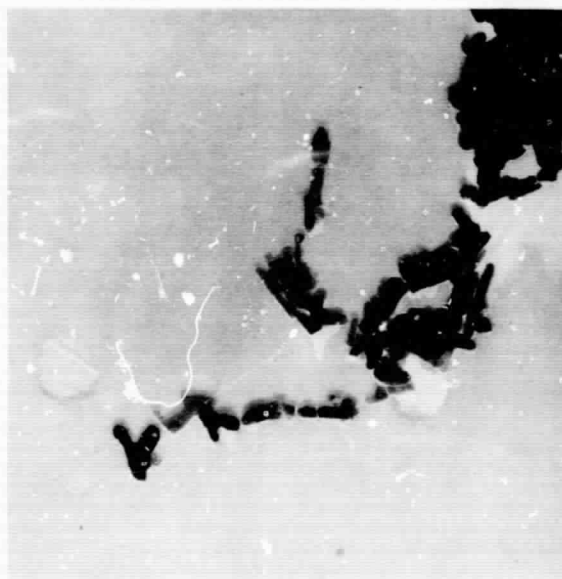
e. Tape 593F (30,000 x Magnification)



f. Tape 606C (30,000 x Magnification)



g. Tape 617 (30,000 x Magnification)

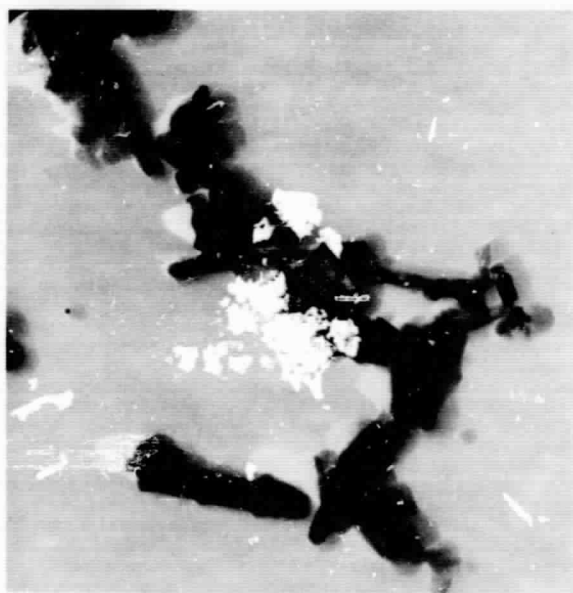


h. Tape 888V (30,000 x Magnification)

Figure 26. Particles Extracted from Various Tapes (Sheet 2 of 3)



i. Tape 991V (30,000 x Magnification)



j. Tape 991GKI (30,000 x Magnification)

Figure 26. Particles Extracted from Various Tapes (Sheet 3 of 3)

Table 1
Observations on Binder Solubility

Binder	Manufacturer	Binder in DMF*	Binder in Acetone	Oxide Dispersion After DMF Treatment**
41-32	RCA	Insoluble	Floats off	Poor
583C	RCA	Soluble	Floats off	Good
593B	RCA	Soluble + AH	Floats off	Poor
593F	RCA	Soluble + AH	Floats off	Good
606C	RCA	Soluble	Floats off	Good
617	RCA	Soluble	Floats off	Good
551 GKI	3-M	Fragments	None	
551 V	3-M	Fragments	None	Poor
591 GKI	3-M	Fragments	None	Poor
591 V	3-M	Fragments	None	Poor
593 B	3-M	Fragments	None	Poor
888 GKI	3-M	Fragments	None	Poor
888 V	3-M	Fragments	None	Poor
991 GKI	3-M	Fragments	None	Poor
991 V	3-M	Fragments	None	Poor

*Dimethyl formamide

**Comparative dispersion in a Branson-ultrasonic cleaner

Table 2
Basic Tape Characteristics

	3-M 551	RCA 617R	3-M 591	RCA 41-32	3-M 951	Memorex 63L	RCA 606A	Memorex 62L
Total tape thickness (mils)	1.2	1.3	1.1	1.1	1.1	1.2	1.1	1.1
Carrier thickness (mils)	1.0	0.9	1.0	0.9	1.0	1.0	0.9	1.0
Binder-oxide thickness (mils)	0.2	0.4	0.1	0.2	0.1	0.2	0.2	0.1
Percent iron oxide	78.1	81.3	67.3	71.4	74.5	80.0	81.6	73.2
Percent binder (approximate)	21.9	18.7	32.7	29.6	25.5	20.0	18.4	26.8
Iron-oxide/binder ratio (approximate)	3.5	4.4	2.1	2.4	2.9	4.0	4.4	2.7
Iron-oxide particle size range	0.01 μ 0.3 μ	0.2 μ 1.0 μ	0.3 μ 1.0 μ	0.01 μ 0.5 μ		0.2 μ 1.0 μ	0.3 μ 1.0 μ	0.2 μ 1.0 μ
Carbon in binder		+					+	
*Rough surface texture, peak-to-peak (mu)	1000.0 50.0 50.0	50.0 100.0 100.0	100.0 125.0 150.0	25.0 25.0 25.0	90.0 160.0 70.0	200.0 150.0 175.0	75.0 100.0 300.0	100.0 50.0 200.0
Center-line average fine texture	2.4 4.0	6.0 6.0	7.0 10.0	8.1 4.8	3.0 3.5	7.0 5.0	4.5 4.5	6.0 2.5
$\lambda = 0.03$ inches	2.0	6.0	6.0	5.2	3.0	3.5	5.0	6.0

λ = cut off wavelength in inches

*Tests performed with a Talysurf 4-profilometer. Three separate runs were made on each tape for rough texture and fine texture at ambient temperature.

Table 3
Major Diffraction Lines Common to γ -Fe₂O₃ and Fe₃O₄

γ -Fe ₂ O ₃		Fe ₃ O ₄	
d	Intensity	d	Intensity
4.84	40	4.85	40
2.95	100+	2.97	70
2.52	100+	2.53	100
2.41	8	2.42	10
2.09	100+	2.10	70
1.70	100+	1.71	60
1.61	100+	1.60	85

Table 4
Data Obtained from Examination of Oxide Particles

Tape Number	Particle Size	Color	Shape
583C*	0.2 - 1.0 μ	Lt. Brn.	Acicular
606C*	0.3 - 1.0 μ	Dk. Brn.	Acicular
593F	0.2 - 0.5 μ	Brn.	Acicular
591GKI	0.3 - 1.0 μ	Lt. Brn.	Acicular
593B	0.2 - 0.5 μ	Brn.	Acicular
888V	0.1 - 0.5 μ	Dk. Grey	Acicular
991GKI	0.2 - 1.5 μ	Dk. Brn.	Acicular
991V	0.2 - 1.0 μ	Dk. Brn.	Acicular
617*	0.2 - 1.0 μ	Lt. Brn.	Acicular
591V	0.2 - 1.5 μ		Acicular

*583C, 606C, and 617 had graphite in the binder-oxide layer.

Table 5
Comparative Emission Spectrographic Analysis of Iron Oxide Separated
from RCA 617 Binder and Iron Oxide in Combination with 617 Binder

Iron Oxide Without Binder	Iron Oxide With Binder
Fe >10%	Fe >10%
Zn 0.01 - 0.1%	Zn 0.01 - 0.1%
Cu 0.003 - 0.03%	Cu 0.003 - 0.03%
Sn 0.0001 - 0.001%	Sn 0.0001 - 0.001%
Ni 0.0003 - 0.003%	Ni 0.0003 - 0.003%
Al 0.003 - 0.03%	Al 0.003 - 0.03%
Si 0.0001 - 0.001%	Si 0.01 - 0.1% (Only difference)
Cr 0.0003 - 0.003%	Cr 0.0003 - 0.003%
Mn 0.0003 - 0.003%	Mn 0.0003 - 0.003%
Mg 0.0001 - 0.001%	Mg 0.0001 - 0.001%
Ca 0.0001 - 0.001%	Ca 0.0001 - 0.001%
Ti 0.0003 - 0.003%	Ti 0.0003 - 0.003%
Pb 0.0001 - 0.001%	Pb 0.0001 - 0.001%
Co not detected	Co not detected